

PHASE TRANSFORMATIONS IN RUBIDIUM NITRATE AND ITS  
SOLID SOLUTIONS WITH CESIUM AND POTASSIUM NITRATES

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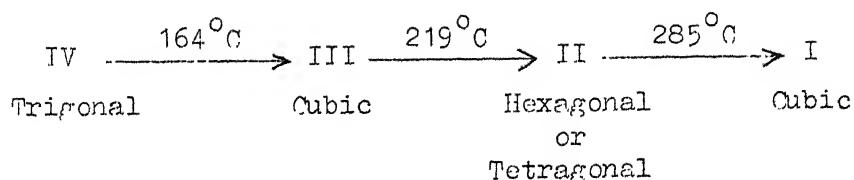
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## PREFACE

Rubidium Nitrate ( $\text{RbNO}_3$ ) exists in four crystalline phases as follows:



Phase transformations in Rubidium Nitrate and its solid solutions with Cesium Nitrate and Potassium Nitrate are the subject of this thesis

The thesis contains five chapters and seven appendices.

Chapter 1 reviews the relevant literature

Statement of the problem is given in Chapter 2.

The experimental techniques employed in the present investigation are: (ac) electrical conductivity, differential thermal analysis (DTA), linear and axial thermal expansion, X-ray diffraction, and infrared absorption. These are described in Chapter 3.

The results of the investigation are compiled in Chapter 4. The transformation temperatures, in  $\text{RbNO}_3$  and its solid solutions, are marked by discontinuous changes in electrical conductivity and lattice parameters. Temperature hysteresis, in



the transformation regions, is observed by all the present experiments. A systematic study of the phases IV, III, II and I of  $\text{RbNO}_3$  is presented. Phase I, which was not clearly detected before by electrical methods, is detected unambiguously by electrical conductivity, dilatometric, and infrared absorption studies. It was also confirmed by X-ray diffraction and differential thermal analysis. The following data are tabulated.

1. Conductivity experiment: activation energy of conduction in different phases of  $\text{RbNO}_3$ ,
2. Differential Thermal Analysis: thermal activation energy, and heats of transformations,
3. Dilatometric experiment: percent changes in length at the phase changes and coefficients of linear thermal expansion in the stable phases,
4. X-ray studies: Coefficients of thermal expansion in stable phases, and percent volume and axial changes at the phase transitions.

Potassium Nitrate is observed to go into solid solutions in Rubidium Nitrate to an extent of  $\sim 5$  mole percent and Cesium Nitrate to an extent of  $\sim 25$  mole percent at room temperature. Partial substitution of Cesium ion (radii of  $\text{Cs}^+$  and  $\text{Rb}^+$  ions are  $1.68\text{\AA}$  and  $1.48\text{\AA}$  respectively) for Rubidium ion in  $\text{RbNO}_3$  shifts the transition temperature  $\text{III} \rightleftharpoons \text{II}$  markedly to higher temperatures while substitution of Potassium

ion (radius of  $K^+$  is  $1.33 \text{ \AA}$ ) depresses it, more during cooling than during heating. The transition temperatures  $IV \rightleftharpoons III$  and  $II \rightleftharpoons I$  are not much affected. The (composition-temperature) phase-diagram of the solid solution series  $K_xRb_{1-x}NO_3$  and  $Ca_xRb_{1-x}NO_3$  on the Rubidium rich side, are plotted from the conductivity data. These diagrams compare well with those of Kentsler. The results of X-ray diffraction studies—lattice parameters as a function of temperature, detection of phase changes, and co-existence of phases III and II in the transition region  $III \rightleftharpoons II$ ,—are described. Infra-red absorption spectra of  $RbNO_3$  in the temperature range, room temperature to near its melting point, is studied in the frequency range  $700\text{cm}^{-1}$  to  $5000\text{cm}^{-1}$ . The spectra are presented in the range 700 to  $1200\text{cm}^{-1}$ , as this covers the fundamental frequencies of the  $NO_3^-$  ion. While no spectrum was observed in phase II, the spectra observed in all other phases were essentially due to the  $NO_3$  groups. Infra-red spectra of solid solutions at room temperature are also presented.

The results described above are synthesized in Chapter 5. The experimental results of Chapter 4, taken together with the available data in the literature, make it possible to suggest an

atomistic approach for understanding the phase transformations in  $\text{RbNO}_3$ . Infra-red absorption spectra in different phases of  $\text{RbNO}_3$  are discussed in terms of the disordering of  $\text{NO}_3$  groups. The absence of spectra in phase II has been associated with the ordering of  $\text{NO}_3$  groups. The increase in electrical conductivity at  $\text{IV} \rightarrow \text{III}$  transformation is associated partly with the orientational disordering of the  $\text{NO}_3^-$  ions and partly with the positional randomization of  $\text{Rb}^+$  ions. The decrease in conductivity at  $\text{III} \rightarrow \text{II}$  transition has been interpreted as due to the ordering of the  $\text{NO}_3^-$  ions. The gradual disordering of the  $\text{NO}_3^-$  ions at  $\text{II} \rightarrow \text{I}$  transition has been considered responsible for this gradual order-disorder transformation. Orientational effects are proposed to explain the difference in results, obtained from dilatometric measurement of bulk expansion and X-ray measurement of axial expansion, after  $\text{III} \rightarrow \text{II}$  transformation. The shifting of transformation temperatures, by the partial ionic substitutions in solid solutions, is explained on the basis of thermal activation energy values obtained from DTA and the similarity of phases IV and III of  $\text{RbNO}_3$  with II and I of  $\text{CsNO}_3$  and phase II of  $\text{RbNO}_3$  with I of  $\text{KNO}_3$ . Thermal hysteresis is explained on the basis of co-existence of phases in the transformation regions. Phase II of  $\text{RbNO}_3$  is found to have a hexagonal symmetry rather than tetra-

gonal. A possible structure for phase II is proposed and the cation positions are indicated. The lattice relationships are proposed for the different phases of  $\text{RbNO}_3$ .

Appendices A, B, and C give the derivation of the expressions used for the calculations of heats of transition, thermal energies of activation in DTA experiment and magnification in the dilatometric experiment respectively. Appendices D, E, F and G list the data obtained from electrical conductivity measurements, DTA, dilatometric and X-ray studies respectively.

## INTRODUCTION

Alkali metal nitrates except  $\text{LiNO}_3$  exhibit polymorphic transformations. Phase transformations in alkali nitrates have been reviewed by Cleaver et al<sup>1, 2</sup> and McLaren<sup>3</sup>. This thesis describes the phase transformations in Rubidium Nitrate and its solid solutions with Cesium Nitrate and Potassium Nitrate.

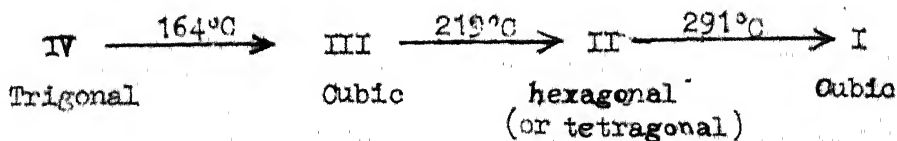
### 1.1 Crystal Growth

Needle shaped crystals of  $\text{RbNO}_3$  with triangular cross-section were grown from an aqueous solution at room temperature by Brown and McLaren<sup>4</sup>. Kennedy<sup>5</sup> grew crystals of  $\text{RbNO}_3$  from the melt.

$\text{RbNO}_3$  was purified by zone-melting method by Sue et al<sup>6</sup>.

### 1.2 Phase Transformations

X-ray diffraction patterns of  $\text{RbNO}_3$  do not show any structural changes between liquid nitrogen temperature and room temperature<sup>7</sup>. Above room temperature  $\text{RbNO}_3$  has the following four crystalline forms<sup>8,9</sup>.



Form IV crystallizes from aqueous solution at room temperature as needles with triangular cross section. X-ray photographs<sup>4</sup> show that IV is trigonal with  $a = 10.48 \text{ \AA}$  and  $c = 7.45 \text{ \AA}$ . The needle axis corresponds to the  $c$  - axis and the sides of the triangular cross-section are parallel to the  $a$  - axis. The space group is  $P3_112$  or  $P3_212$  (i.e.  $D_3^4$  or  $D_3^6$ ).

Form III is cubic<sup>4,10</sup> with  $a = 4.36 \text{ \AA}$  and  $Z = 1$ . Korhonen<sup>11</sup> on the basis of x-ray powder photographs at  $190^\circ\text{C}$ . suggests that the true unit cell of  $\text{RbNO}_3$  is cubic with  $a = 8.74 \text{ \AA}$ . Korhonen<sup>11</sup> gave the space group as  $T_h^6 - Pa3$  while Finbak and Hassel<sup>10</sup> suggested  $O_h^1 - Pm3m$ . The atomic positions are : eight Rubidium ions at cell corners, cell center, cell face centers and cell edge centers; eight Nitrogen ions on cell body diagonals at  $uuu$  with  $u = 0.285$ , and twenty-four oxygen ions at  $xyz$  etc with  $x = y = 0.278$  and  $z = 0.399$  (fig 1.1).  $\text{NO}_3^-$  was assumed to be symmetrical with  $\text{N-O} = 1.22 \text{ \AA}$ . Finbak and Hassel<sup>10</sup> suggested that  $\text{NO}_3^-$  ions are in free rotation in form III, whereas Korhonen<sup>11</sup> believes that  $\text{NO}_3^-$  ion disorder is similar to that suggested by Fischmeister<sup>12</sup> in  $\text{KNO}_3$ .

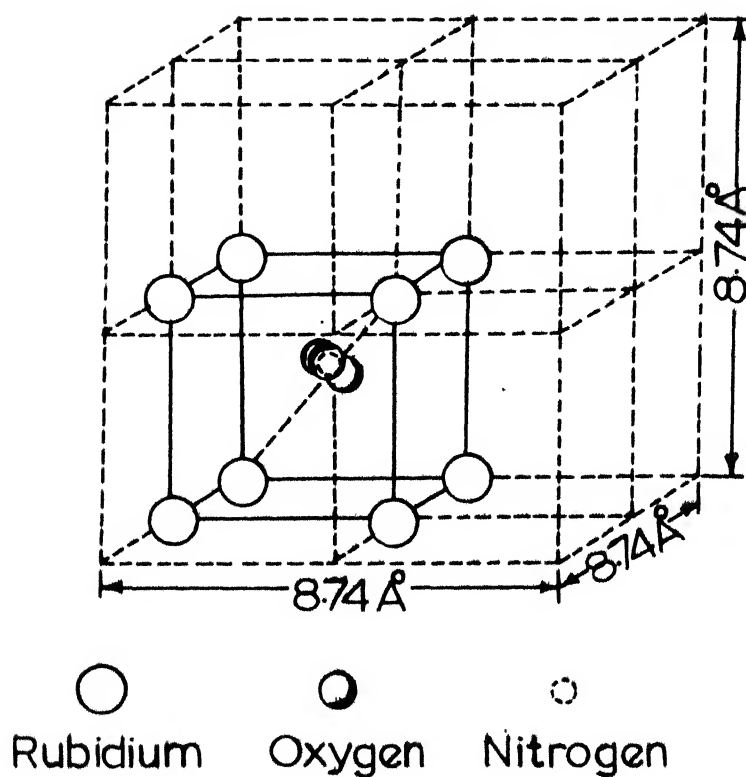


FIG. 1.1 Unit cell of form III of Rubidium Nitrate with atomic positions in  $1/8$  th of the unit cell (constructed after ref. 11).

X-ray photographs of single crystals heated through IV  $\rightarrow$  III transformation, show that the trigonal  $[00.1]$  of IV transforms to cubic triad  $[111]$  of III<sup>4,13,14</sup> with the trigonal  $[10.1]$  direction becoming the cubic edge  $[100]$ <sup>4</sup>. The structural relationship<sup>4</sup> between phases IV and III is shown in fig. 1.2.

After III  $\rightarrow$  IV transition, any one of the four equivalent cube diagonals can become the trigonal c - axis. Therefore in the transformation cycle IV  $\rightarrow$  III  $\rightarrow$  IV, the crystals may come back to form IV in any one of the four orientations. For a needle crystal of triangular cross-section, it is possible to calculate<sup>4</sup> the angle between the needle axis and the crystallographic c - axis corresponding to each of the four possible orientations. These angles are 0°, 70.5°, 55° and 55° (two cube diagonals are indistinguishable). All these orientations were observed by Brown and McLaren<sup>4</sup> under the microscope.

On the basis of powder photographs Brown and McLaren<sup>4</sup> found several possible cells for form II : the most probable being tetragonal with  $a = 6.19\text{\AA}$ ,  $c = 8.74\text{\AA}$  and  $Z = 4$ . Finbak et al<sup>13</sup> gave the unit cell of II as hexagonal with  $a = 5.48\text{\AA}$ ,  $c = 10.71\text{\AA}$ .



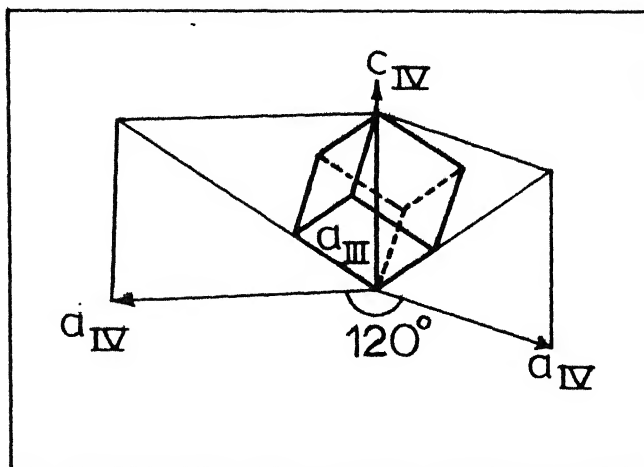


Fig. 1.2 Structural relationship between the unit cells of forms IV and III of Rubidium Nitrate (ref. 4).

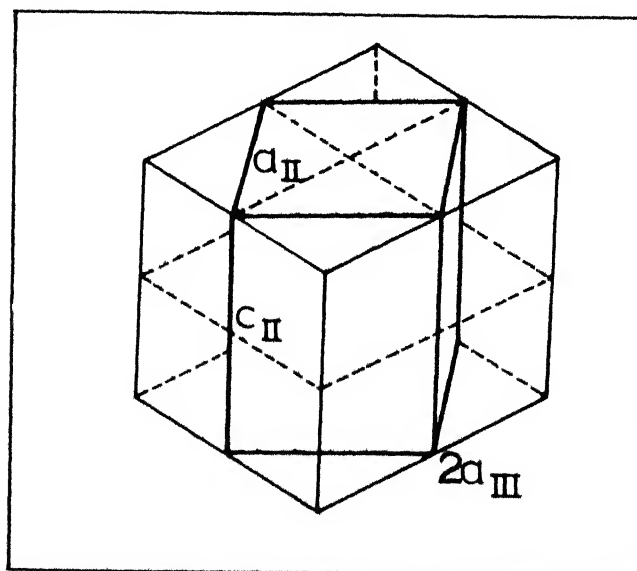


Fig. 1.3 Structural relationship between the unit cells of forms III and II of Rubidium Nitrate (ref. 4).

At  $\text{III} \longrightarrow \text{II}$  transformation the crystals are observed to crack and bend and become anisotropic. Distortion of crystals increases on cooling. Due to this distortion Brown and McLaren could not study these (and  $\text{II} \rightleftharpoons \text{I}$ ) transformations on single crystals with x-rays. This transformation was therefore studied by powder diffractometry<sup>4</sup>.

Although there are several possible unit cells for II, the dimensions of unit cell of III and the most probable unit cell of II show a simple relation (fig. 1.3), namely

$$\sqrt{2} a_{\text{III}} = 6.16 \text{ \AA}, a_{\text{II}} = 6.19 \text{ \AA}$$

$$2 a_{\text{III}} = 8.72 \text{ \AA}, c_{\text{II}} = 8.74 \text{ \AA}$$

This suggests that the true unit cell of II is tetragonal<sup>4</sup> (with  $a = 6.19 \text{ \AA}$ , and  $c = 8.74 \text{ \AA}$ ). Therefore, at  $\text{III} \longrightarrow \text{II}$  transformation the crystal has a choice of three possible orientations, corresponding to three mutually perpendicular directions for  $c_{\text{II}}$  - axis. The choice of orientations may be responsible for the fragmentation which occurs at this transformation<sup>4</sup>.

X-ray powder photographs show that phase I has NaCl structure<sup>5</sup>. Brown and McLaren<sup>4</sup> on the basis of x-ray diffractometer pattern show that form I is cubic with  $a = 7.32 \text{ \AA}$ ,  $Z = 4$ . The  $\text{II} \longrightarrow \text{I}$  transformation was observed under the microscope, the crystals becoming isotropic without any extra distortion or fragmentation being evident<sup>4</sup>.

However, no simple relation between the cell dimensions of II and I was found. Based on the gradual changes in x-ray reflections at  $II \rightleftharpoons I$  transformation, Kennedy<sup>5</sup> has suggested an order-disorder transition in the anion arrangement ~~general view is of nature, remaining unaltered.~~ with ~~no change in the~~  $Rb^+$  positions. Since the temperature of this transformation is only 20°C below the melting point, it is possible that crystals are sufficiently plastic to withstand a structural change in which  $a_{II}$  and  $c_{II}$  expand and contract respectively, to become equal to  $a_I^{(4)}$ . Kennedy<sup>5</sup> has reported that the crystal decomposes during long x-ray exposures and therefore moving film methods could not be applied to verify the structure of form I.

### 1.3 Electrical Conductance

Brown and McLaren<sup>4</sup> have measured the electrical conductance of compressed powder pellets of  $RbNO_3$  as a function of temperature. DC methods were employed for temperatures upto about 250°C and a frequency of 1 KC/S for measurements above 250°C. The results of these measurements, shown in fig 1.4, indicate the following : (i) at  $IV \rightarrow III$  transformation conductance increases by a factor of 100. A corresponding decrease occurs during the reverse transformation. This behaviour is repeatable.

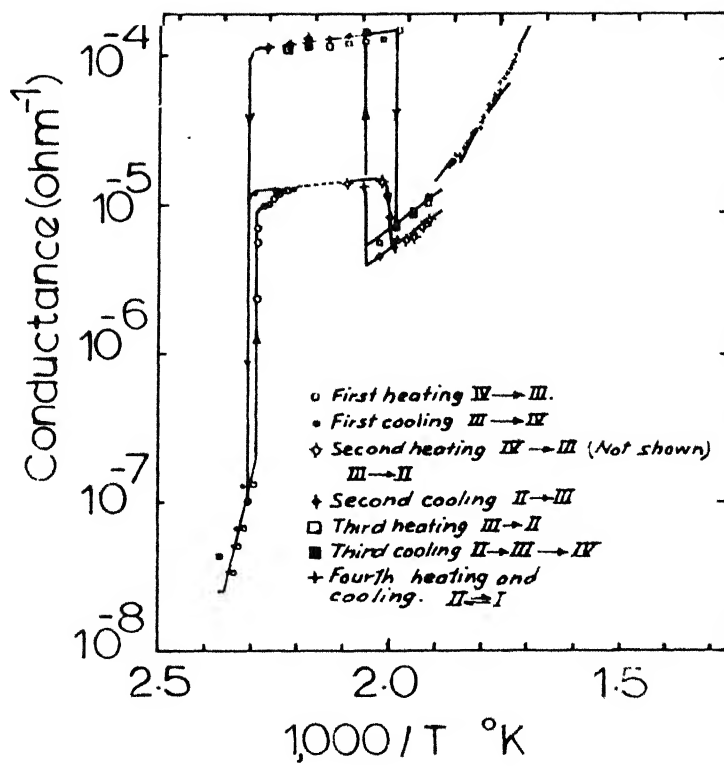


Fig. 1.4 The electrical conductance of Rubidium Nitrate as a function of temperature (ref. 4).

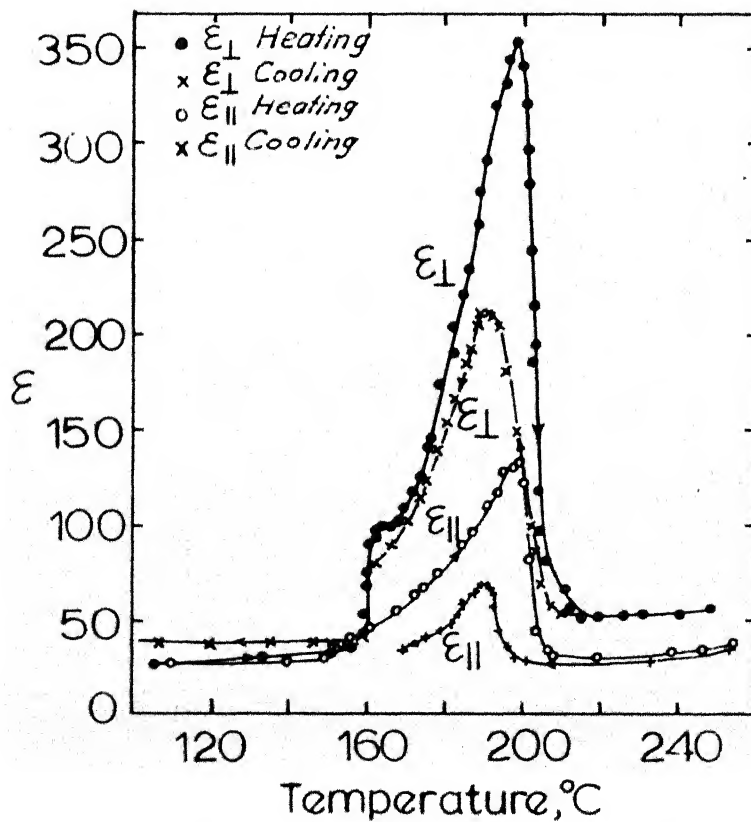


Fig. 1.5 Temperature dependence of  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  of Rubidium Nitrate (rising and falling temperature) (ref. 26).

(ii) The first  $\text{III} \rightarrow \text{II}$  transformation leads to a decrease in conductance by a factor of 3 whereas an increase by a factor of 30 takes place at the reverse transformation. On repeating the  $\text{III} \rightleftharpoons \text{II}$  cycle the conductance changes by a factor of 30 both on heating and cooling. (iii) On further cooling, the conductance decreases by a factor of 1000 at  $\text{III} \rightarrow \text{IV}$  transition to its original value. On reheating the sample, the conductance increases by a factor of 1000 at  $\text{IV} \rightarrow \text{III}$  transition and decreases by a factor of 30 at the  $\text{III} \rightarrow \text{II}$  transformation. This behaviour [(i) to (iii)] was confirmed on a second sample<sup>4</sup>, and (iv) the  $\text{II} \rightleftharpoons \text{I}$  transition involves only a change of slope in the graph of  $\log$  (conductance) against reciprocal absolute temperature.

The conductance changes at  $\text{II} \rightleftharpoons \text{I}$  transformations were interpreted by Brown and McLaren<sup>4</sup> as an evidence that these transformations do not involve any sudden change in positional randomization of the ions.

It is evident from fig 1.4 that when the transformation involves an increase in crystallographic symmetry, the electrical conductance increases, and vice versa<sup>4</sup>. This has also been observed in  $\text{KNO}_3$ ,  $\text{TLNO}_3$ ,  $\text{CsNO}_3$  and  $\text{NH}_4\text{NO}_3$ . Brown and McLaren<sup>15</sup>

have shown by proton magnetic resonance that the increase in conductance at  $\text{II} \rightarrow \text{I}$  transformation in  $\text{NH}_4\text{NO}_3$ , is due to positional randomization of the  $\text{NH}_4^+$  ions. There is evidence that a similar situation exists in  $\text{TlNO}_3$ <sup>16</sup>. It was, therefore, suggested by Brown and McLaren<sup>4</sup> that the increase in conductance at  $\text{IV} \rightarrow \text{III}$  transformation is due to some positional randomization of the  $\text{Rb}^+$  ions, and that the decrease at  $\text{III} \rightarrow \text{II}$  transformation corresponds to an ordering process.

After the first  $\text{II} \rightarrow \text{III}$  transition a permanent increase in conductance of phase III over its original value was noted<sup>4</sup> (fig. 1.4). This remained unexplained and is now explained in Chapter 5.

After  $\text{IV} \rightarrow \text{III}$  transformation, Kennedy<sup>17</sup> has observed changes in x-ray reflections of phase III on annealing it for more than 20 hours. These changes are paralleled by changes of 20 to 40% in ionic conductivity.

The transport properties of the fused alkali nitrates have been studied by a number of investigators<sup>18-23</sup> using radio tracers. The results pertinent to this study are summarized in table 1.1.

Table 1.1 Transport Properties in Fused Alkali Nitrates.

Species	Diffusion Coefficient, $D \times 10^5 (\text{cm}^2/\text{sec})$	Ionic mobility, $u \times 10^4$ $(\text{cm}^2/\text{v. sec})$	Transport Number
$\text{NO}_3^-$ in $\text{KNO}_3$		$2.45 \pm 0.1^{(22)}$	
$\text{NO}_3^-$ in $\text{RbNO}_3$		$2.38 \pm 0.08^{(22)}$	
$\text{NO}_3^-$ in $\text{CsNO}_3$		$2.38 \pm 0.06^{(22)}$	
$\text{K}^+$ in $\text{RbNO}_3$	$2.14 \pm 0.12^{(22)}$ $2.52 \pm 0.10^{(23)}$	$2.33 \pm 0.05^{(22)}$	
$\text{Rb}^+$ in $\text{RbNO}_3$	$2.24 \pm 0.05^{(22)}$ $2.51 \pm 0.08^{(23)}$	$2.26 \pm 0.036^{(22)}$	$0.56 \pm 0.03^{(19)}$ ; $0.38^{(20)}$ ; $0.59 \pm 0.04^{(21)}$
$\text{Cs}^+$ in $\text{RbNO}_3$	$2.29 \pm 0.07^{(22)}$	$2.24 \pm 0.036^{(22)}$	
$\text{K}^+$ in $\text{KNO}_3$	$3.21 \pm 0.20^{(22)}$	$3.12 \pm 0.05^{(22)}$	$0.59 \pm 0.02^{(21)}$
$\text{Cs}^+$ in $\text{CsNO}_3$	$2.29 \pm 0.07^{(22)}$	$2.30 \pm 0.025^{(22)}$	$0.50 \pm 0.04^{(19)}$ ; $0.40^{(20)}$ ; $0.59 \pm 0.07^{(21)}$

22 Values of  $u$  and  $D$  recorded here are obtained from the plots of  $u$  or  $D$  vs cationic radii for alkali nitrates. These values were measured at  $450^\circ\text{C}$ .

The logarithm of viscosity ( $\eta$ ) of molten alkali nitrates was found to vary linearly with the reciprocal of absolute temperature<sup>24</sup>. For these materials,  $\sigma^n \eta = \text{constant}$  where  $\sigma$  is the electrical conductivity and  $n$  represents the ratio of activation energies for viscous flow and electrical conduction.

#### 1.4 Dielectric Properties

Dantsiger<sup>25, 26</sup> and Fesenko<sup>26</sup> have measured the dielectric constants parallel ( $\epsilon_{||}$ ) and perpendicular ( $\epsilon_{\perp}$ ) to the trigonal axis for  $\text{RbNO}_3$  at a frequency of 1Mc/s as a function of temperature. Both the dielectric constants have an anomalous behaviour, particularly  $\epsilon_{\perp}$  (fig 1.5, p.8). It is evident from fig 1.5 that there is a discontinuity in  $\epsilon_{\perp}$  at IV  $\rightarrow$  III transition and a sharp peak in  $\epsilon_{\perp}$  at the III  $\rightarrow$  II transition.

The changes in  $\epsilon_{\perp}$  were compared with those in conductivity at the phase transitions as shown below.

Transition	Dielectric constant $\epsilon_{\perp}$	Electrical conductivity
IV $\rightarrow$ III	Increases by a factor of 3	Increases by a factor of 100
III $\rightarrow$ II	Increases by a factor of 10	Decreases by a factor of 30

The above comparative study and the fact that above III  $\rightarrow$  II transition  $\epsilon_{\perp}$  falls nearly to its initial value (fig 1.5) show that the behaviour of  $\epsilon_{\perp}$  does not follow that of conductivity.

On the basis of crystallographic criterion for spontaneous polarisation Zheludev and Sonin<sup>27</sup> (and on the dielectric and dilatometric measurements, Dantsiger<sup>25</sup>) proposed  $\text{RbNO}_3$  as a probable ferroelectric. However, the space group



symmetry of  $\text{RbNO}_3$  crystals was found not to obey the more precise crystal physical criterion<sup>28, 29</sup>. Protzenko et al<sup>30</sup> were also unable to find any ferroelectric properties in single crystals of  $\text{RbNO}_3$ . On the basis of the study of the dielectric properties of (i) crystals and (ii) cooled melt of  $\text{RbNO}_3$  Dantsiger and Fesenko<sup>26, 31</sup> have found and confirmed the antiferroelectric properties for phases II and IV. In comparison with the ferroelectric properties of  $\text{KNO}_3$ <sup>32</sup> Dantsiger and Fesenko<sup>26</sup> associate the antiferroelectric behaviour of phase II in  $\text{RbNO}_3$  with rotation (about the principal axis) and antiparallel displacement of  $\text{NO}_3$  groups within any one domain.

Rinbak and Hassel<sup>33</sup> report that phase IV of  $\text{RbNO}_3$  is pyroelectric.

## 1.5 Thermal Expansion

Using a quartz dilatometer Dantsiger<sup>25, 26</sup> and Fesenko<sup>26</sup> have measured the coefficients of thermal expansion for the directions parallel and perpendicular to the three fold axis ( $l_{11}$  and  $l_{\perp}$ ) of  $\text{RbNO}_3$ . Fig. 1.6 shows  $\frac{l-l_0}{l_0}$  for these two directions as a function of temperature ( $l_0$  is the length at  $20^\circ\text{C}$ ). It is evident that the coefficients for  $l_{11}$  and  $l_{\perp}$  are positive for phase IV. On the other hand, the coefficients are negative for phase III, especially for  $l_{\perp}$  at  $\text{IV} \rightarrow \text{III}^*$ , and  $\text{III} \rightarrow \text{II}$  transition points.

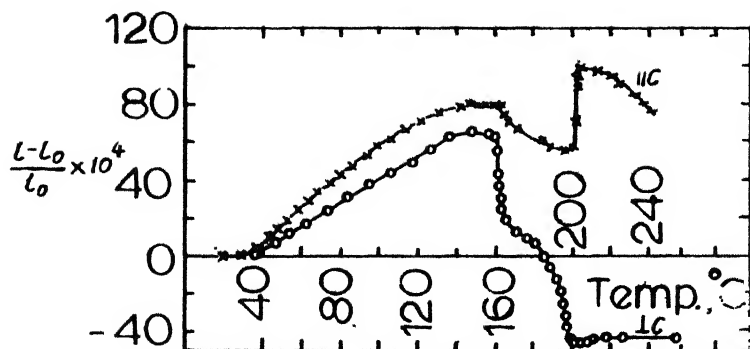


Fig. 1.6 Thermal expansion as a function of temperature for two directions of Rubidium Nitrate (ref. 26).

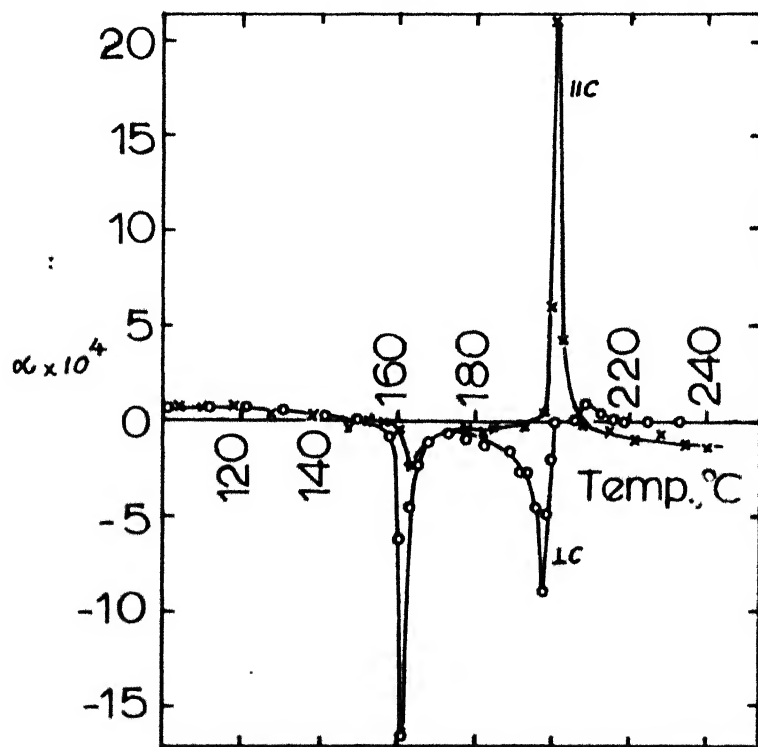


Fig. 1.7 Coefficients of thermal expansion of Rubidium Nitrate as functions of temperature (ref. 26).

There is a stepwise expansion along  $\ell_{\parallel}$  at III  $\rightarrow$  II transition.

Fig. 1.7 shows the coefficients  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  as a function of temperature. The transition points stand out as sharp peaks.

Kennedy<sup>17</sup> has reported, on the basis of single crystal x-ray diffractometry, that the coefficient of thermal expansion for phase III is positive (Table 1.2). Table 1.2 lists thermal data for stable phases and table 1.3 gives the volume changes at the phase transitions of  $\text{RbNO}_3$ . The density and molar volume of fused alkali nitrates including  $\text{RbNO}_3$  were determined by Protzenko et al<sup>18</sup>. The density was found to vary linearly with temperature.

Recently Rapoport<sup>34</sup> has investigated IV  $\rightleftharpoons$  III transformation in  $\text{RbNO}_3$  upto 40 Kilobars (Kb). DTA signals were obtained with no hysteresis upon cooling. Bridgman<sup>35</sup> found new polymorphs in  $\text{RbNO}_3$  above 17 kb. Some similarities in the phase diagrams of  $\text{RbNO}_3$ ,  $\text{CsNO}_3$  and  $\text{TlNO}_3$  were pointed out in the early work of Bridgman<sup>36</sup>. Recently Rapoport and Kennedy<sup>37</sup> have suggested that the phase diagrams of  $\text{KNO}_3$  above 15 kb,  $\text{RbNO}_3$  above 2 kb and  $\text{CsNO}_3$  are qualitatively similar and that the corresponding phases are isostructural. The isoelectronic solids

TABLE 1.2 Thermal data for  $\text{PbNO}_3$  (ref. 2)

Crystal structure	Temperature range (°C)	Molar volume (c.c.)	Density (gr/c.c.)		Volume thermal expansion coeff. $\alpha \times 10^{-6}$ (°C) <sup>-1</sup>	$\alpha \times 10^{-6}$ (°C) <sup>-1</sup>	Specific heat $C_p$ ** (cal/g) <sup>44</sup>
			observed <sup>38</sup>	calculated <sup>4</sup>			
Trigonal	20 to 162	47.2	3.11 (room temp.)	3.11 (room temp.)	210	101.5*	97.1*
							0.1567 ± 2.76 × 10 <sup>-4</sup> t <sub>+</sub> 0.0009 (50-160°C)
Cubic	162 to 220	49.6	-	2.96 (at 180°C)	340	85.0*	0.1864 ± 4.73 × 10 <sup>-4</sup> t <sub>+</sub> 0.0022 (160-220°C)
Hexagonal	220 to 281	56.9	-	2.92 (at 220°C)	-	-	0.2445 ± 1.12 × 10 <sup>-4</sup> t <sub>+</sub> 0.001 (220-281°C)
Cubic	281 to 310	59.0	-	2.50 (at 295°C)	-	-	0.2650
Melt	312 to above	59.33 <sup>***</sup>	-	-	405 <sup>3</sup>		0.2143 ± 1.37 × 10 <sup>-5</sup> t <sub>+</sub> 0.0016 (310-350°C)

\*\*\* Molar volume before melting is 59.47 c.c and after melting is 59.33 c.c.<sup>39</sup>

\*\* In the last column the temperature range (t) is given in brackets. Phase I exists over such a narrow range that there is no significant change from the value given.

\* These expansion coefficients were obtained from an X-ray study of single crystals.<sup>17</sup>

TABLE 1.3 Thermodynamic Parameters of Phase transitions of  $\text{RbNO}_3$  44,45,47

Transition	$\Delta V$ c.c./mole	Heat of transition (cal/mole)	Entropy of transition ( $\Delta S$ ) (cal/mole deg)	$\Delta S = R \ln N$ cal/mole deg.
ref. 2	ref. 47	ref. 44	ref. 44	ref. 45
IV $\rightarrow$ III	(+2.4)* +2.52	932 $\pm$ 1.5% 923 $\pm$ 1.5% 950 $\pm$ 15%	2.15 $\pm$ 1.5%	2.11 2.18(3)
III $\rightarrow$ II	(+5.0)* +6.00	767 $\pm$ 2.0% 774 $\pm$ 1.5% 650 $\pm$ 15%	1.53 $\pm$ 2.0%	1.57 2.11 + 1.57 = 3.68 3.56(6)
II $\rightarrow$ I	(+0.5)* +3.12	230 $\pm$ 6.5% - 300 $\pm$ 15% 0.42 $\pm$ 6.5%	-	3.68 $\pm$ 0.42 = 4.10 4.13(8)
I $\rightarrow$ liquid	- (0.14) (35) <sup>ⓐ</sup> -(0.36) (42)	1109 $\pm$ 1.5% - - 1.90 $\pm$ 1.5%	-	-

\* Dilatometric values for  $\text{RbNO}_3$  show discrepancies (cf refs 2 and 13)

\*\*  $\Delta S$ , at the phase transitions, is regarded as configurational entropy. It is assumed that configurational entropy of phase IV is zero. Thus values of  $\Delta S$  in this column are values of entropy of phases IV, III, II and I. A value close to these with a definite value of  $N$ , written in the bracket, is also recorded.

ⓐ Value of  $\Delta V$  observed in reference 39, at I  $\rightarrow$  liquid was improved later in ref. 42.

$\text{RbNO}_3$  and  $\text{SrCO}_3$  allow interesting comparison of corresponding crystal structures and phase diagrams<sup>34</sup>.

The melting points and the volumes of fusion of alkali nitrates including  $\text{RbNO}_3$  were determined, at pressures upto 10 kb, by Owens<sup>43</sup>. There is a striking similarity in the melting curves of  $\text{CsNO}_3$ ,  $\text{RbNO}_3$  above 2 kb and  $\text{KNO}_3$  (phase VI)<sup>35</sup> which again suggests that the corresponding solid phases are isostructural.

#### 1.6 Specific Heat, Heats of Transitions, Entropy and Free-Energy.

Mustajoki<sup>44</sup> has determined the specific heats of various phases of  $\text{RbNO}_3$  with a Moser calorimeter using both heating and cooling curves. These are tabulated in table 1.2

Heats of transition and entropy of transition as determined by Mustajoki<sup>44</sup> and Arell and Varteva<sup>45</sup> are summarized in table 1.3.

Gordon and Campbell<sup>46</sup> have studied the crystalline transitions and fusion of alkali nitrates including  $\text{RbNO}_3$  by differential thermal analysis (DTA). Rao and Rao<sup>47</sup> have also recently examined the phase transformations of alkali nitrates by DTA. The values of heats of transition and of volume changes, from the DTA study<sup>47</sup> seem to be in reasonable agreement with the calorimetric values<sup>44,45</sup> except that the changes in volume at  $\text{II} \rightarrow \text{I}$

Vasil'ev and Vasil'eva<sup>48</sup> have expressed the available data on entropy of the crystal lattice of nitrates by the relation

$$\Delta S_{latt} = \alpha \sum n$$

where  $n$  is the number of ions forming the compounds and  $\alpha$  is a constant. The values of entropies of transition, in the nitrates of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ag}^+$ , and  $\text{Tl}^+$  have been considered in terms of the orientational disorder of  $\text{NO}_3^-$  ion<sup>49</sup>. The data on these nitrates have been discussed in terms of the structural relations for the transitions.

Free energy of the lattice is calculated by the relation

$$\Delta F_{latt} = U - T \Delta S_{latt}.$$

where  $U$  is the lattice energy.

Lattice energies and free energies of  $\text{RbNO}_3$  were calculated by Ladd and Lee<sup>50</sup>.

### 1.7 Infrared Absorption

Infrared absorption spectra of metal nitrates including  $\text{RbNO}_3$ , in the range  $5000 \text{ cm}^{-1}$  to  $700 \text{ cm}^{-1}$  at room temperature has been tabulated by Vranty<sup>51</sup>.

Infrared absorption spectra of single crystals of inorganic nitrates including  $\text{RbNO}_3$  between room temperature and liquid helium temperature were obtained by Schroeder, Weir and Hippincott<sup>7</sup>. Diffuse absorption between  $1400 \text{ cm}^{-1}$  and  $700 \text{ cm}^{-1}$

was observed at room temperature. At liquid helium temperature, this was resolved into a large number of bands which are not attributable to fundamental frequencies ( $\nu_1, \nu_2, \nu_3$ , and  $\nu_4$ ) or combinations of fundamental frequencies of the  $\text{NO}_3^-$  ion. Almost all of these bands were interpreted as summation bands of fundamental frequencies with successive levels of a librating oscillator. The libration is considered to represent a planar torsional oscillation of the anion about the trigonal axis. The librating frequency depends in part on the crystal structure and decreases with increasing cation mass. The librating frequency as determined from successive bands was reasonably constant. In  $\text{RbNO}_3$  two modes were observed one at  $25 \text{ cm}^{-1}$  and the other at  $30 \text{ cm}^{-1}$ . Band limits observed in the spectra were interpreted as representing rotational energy barriers. The barrier heights were  $146 \text{ cm}^{-1}$  and  $175 \text{ cm}^{-1}$ .

Greenberg and Hallgren<sup>52</sup> have observed the infrared spectra of  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{RbNO}_3$  and  $\text{CsNO}_3$  at room temperature, at  $25^\circ\text{C}$  above and at  $25^\circ\text{C}$  below the melting points of these nitrates. They have reported that the spectra of alkali metal nitrates consist almost exclusively of the frequencies to be associated with the  $\text{NO}_3$  group and are not materially altered in going from solid to liquid state. The shift in observed frequencies



with cation size is as follows. With increasing cation size,

$\nu_4$ ,  $\nu_1$  and  $\nu_3$  frequencies show a general shift to lower values while  $\nu_2$  moves to higher frequencies. Also it has been observed<sup>52</sup> that the fundamental frequencies shift to lower values as the temperature is raised. No uniform change with temperature was detected for the combination and overtone bands.

Myasnikova and Yatsenko<sup>53</sup> have recently examined the infrared spectra of cooled melt of  $\text{RbNO}_3$  at  $\text{IV} \rightarrow \text{III}$  transformation. The band frequency corresponding to the internal vibration  $\nu_3$  of  $\text{NO}_3^-$  ion is found to be shifted by about  $12 \text{ cm}^{-1}$  on passing from phase IV to III.

The contribution of internal vibration  $\nu_3$  of  $\text{NO}_3^-$  ion in  $\text{RbNO}_3$ , to the change in dielectric constant is found to be very small. Therefore the structure vibrations seem to play an important role in giving rise to anomalously large dielectric constants at the phase transition. Shifting of other bands can be explained similarly.

### 1.8 Solid Solutions.

The systems of interest in the present study are the solid solutions  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  and  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$ . Hence a literature study of these is described in this section.

### 1.8.1 $K_xRb_{1-x}NO_3$ system

The series  $K_xRb_{1-x}NO_3$  is said to form a solid solution for the whole range of concentration<sup>54,55</sup>. Kawabe et al<sup>56,57</sup> have studied the dielectric properties of the  $K_xRb_{1-x}NO_3$  mixed crystals on the Potassium rich side. They have also investigated the temperature dependence of the lattice parameters of  $K_{0.77}Rb_{0.23}NO_3$ <sup>57</sup> by high temperature x-ray powder diffractometry. At room temperature the x-ray powder diffraction patterns of these mixed crystals show that the lattice parameters vary linearly with concentration<sup>56</sup>. A mixing limit was found at  $x = 0.44$  to  $0.48$ .

Dantsiger<sup>58</sup> has investigated the phase diagram of  $K_xRb_{1-x}NO_3$  system. The Rubidium rich side was studied by dielectric measurements as a function of temperature while the Potassium rich side was investigated by oscillographic measurements only.

The transition  $III \rightarrow II$  during cooling was observed upto 3 - 5 %  $KNO_3$ , while in warming it was observed upto 10 - 15 %  $KNO_3$ <sup>58</sup>. However, the doping lowers the transition temperature and reduces the peak value of  $\epsilon$ . In addition the transition becomes increasingly smeared out. The transition  $IV \rightarrow III$  does not disappear at all. At first it is almost independent of the composition and then, beginning with 10 - 15 %  $KNO_3$  the temperature<sup>58</sup> of the transition decreases. The transition points are shown in fig 1.8. The symbols II, III and IV in the diagram on the

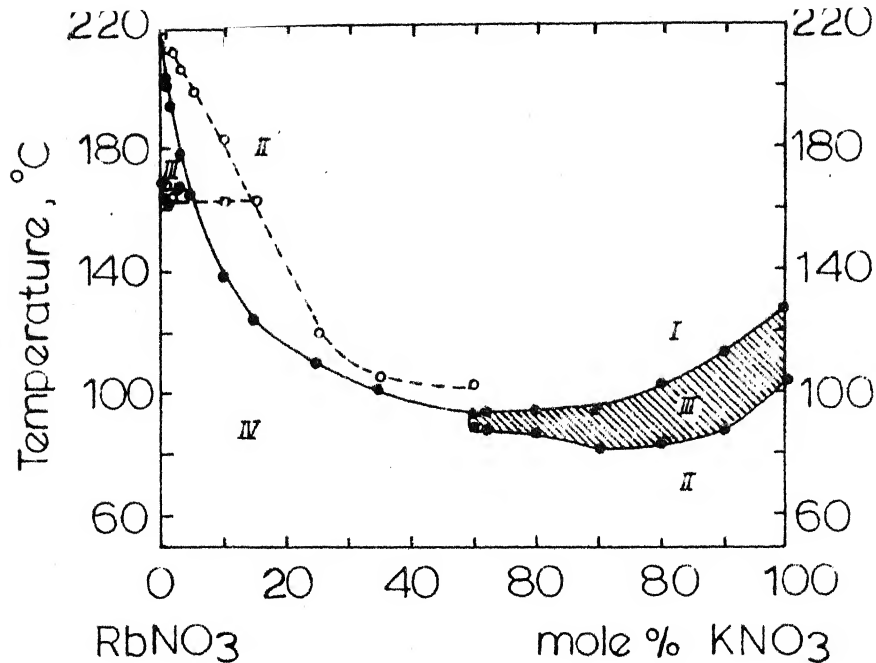


Fig. 1.8 Phase diagram of the  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system. The solid curve corresponds to cooling and the dashed one to heating (ref. 58).

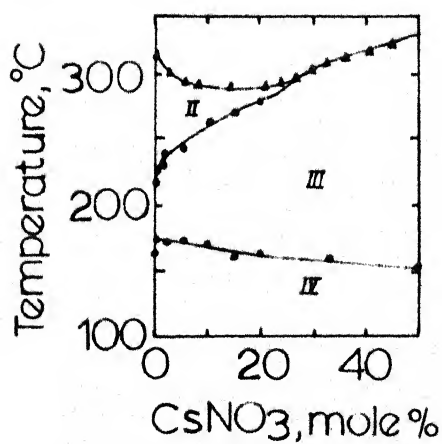


Fig. 1.9 Phase diagram of the system  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  (ref. 61).

RbNO<sub>3</sub> side denote the different phases of RbNO<sub>3</sub>. As was noted above<sup>31</sup> phase IV of RbNO<sub>3</sub> has antiferroelectric properties.

The reasons for this inference were the abrupt jumps in  $\epsilon$  at the IV  $\rightleftharpoons$  III transition, the effects of a dc bias field on this transition and the double hysteresis loops observed in phase IV in strong fields.

In all the investigated solid solutions the anomaly of  $\epsilon$  at IV  $\rightarrow$  III transition temperature persists and double dielectric hysteresis loops are observed in phase IV. Hence it is reasonable to infer the existence of antiferroelectricity in the low temperature phase of the investigated solid solutions<sup>58</sup>, just as in the case of pure RbNO<sub>3</sub>.

Investigation of compositions with a high KNO<sub>3</sub> content<sup>58,59</sup> revealed a ferroelectric region (shaded in the diagram of fig 1.8) In this region there are observed ordinary dielectric hysteresis loops. The symbols I, II and III in the phase diagram on the side of KNO<sub>3</sub> denote the different phases of KNO<sub>3</sub> as identified by Sawada et al<sup>32</sup>. On the KNO<sub>3</sub> rich side the phase diagram proposed by Dantsig<sup>er</sup> (Fig. 1.8) is in reasonable agreement with that of Kawabe et al<sup>56,57</sup>.

### 1.8.2 $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$ System.

This system forms a continuous series of solid solutions.<sup>55,60</sup>

Dantsiger<sup>61</sup> has made (i) dielectric measurements as a function of temperature at a frequency of 1 Mc/S and (ii) oscillographic measurements with the usual Sawyer - Tower circuit on the cooled melts of this system. It was observed from the dielectric data that as  $x$  increases, the transition temperature  $\text{III} \rightleftharpoons \text{II}$  in  $\text{RbNO}_3$  shifts to higher temperatures.

Fig. 1.9 shows the phase diagram of this system, based on the dielectric measurements<sup>61</sup>. The numbers II, III and IV denote the phases of  $\text{RbNO}_3$ . The highest temperature phase I could not be observed during these measurements since the lower boundary of this phase was close to the melting point<sup>61</sup>. The upper curve (fig 1.9) marked by triangles, was plotted from the crystallization temperatures given by Blidin<sup>60</sup>.

It is also noted that<sup>61</sup> (i) transition temperature  $\text{III} \rightleftharpoons \text{II}$  is present throughout the range  $0 < x \leq 0.5-0.20$ , (ii) Curie-Weiss law is followed both below and above this transition temperature and (iii) no hysteresis loop is observed in phase II of the compositions. On the basis of these observations it is concluded that phase II of the solid solutions is antiferroelectric. The possibility that the phase IV of these

compositions is also antiferroelectric (like the phase IV in  $\text{RbNO}_3$ ) is considered. However, the dielectric anomalies in these compositions at IV  $\rightleftharpoons$  III transition, are less pronounced than in pure  $\text{RbNO}_3$ . Dantsiger<sup>61</sup> has proposed that the antiferroelectric properties in phase II of the solid solutions as well as in  $\text{RbNO}_3$  occur as a result of ordering of the  $\text{NO}_3$  groups above the transition temperature.

It can be noted, from section 1.8.1 and the present one, that as  $x$  increases the transition temperature III  $\rightleftharpoons$  II moves to higher temperatures in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system and in the opposite direction in  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system. Dantsiger<sup>61</sup> has explained this shifting of transition temperature on the basis of the difference in the radii of the cations that do the replacing in the solid solutions. The radii of  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{K}^+$  are respectively 1.48, 1.69, and 1.33  $\text{\AA}$ . When  $\text{Cs}^+$  (larger size) replaces  $\text{Rb}^+$ , the lattice constant increases. (According to x-ray data, the lattice constant of  $\text{CsNO}_3$  in cubic phase is larger than the lattice constant of  $\text{RbNO}_3$ <sup>10</sup>). This results in a reduction of the internal field, and, hence in a reduction in the stability and narrowing of the phase II. Replacing  $\text{Rb}^+$  ion by  $\text{K}^+$  ion, which has smaller size, produces the opposite effect.

## Chapter 2

### STATEMENT OF THE PROBLEM

Nitrates show a rich variety of structural transformations, indicating that diverse arrangements with practically the same free energy can be arrived at by comparatively small shifts of the cations and the anions. As already seen in chapter I phase transformations in  $\text{RbNO}_3$  and their solid solutions have been the subject of several investigations.

However, a clear understanding of the transformations in  $\text{RbNO}_3$  does not seem to be available. Due to this reason it is difficult to find proper explanations for the electrical conductivity and thermal expansion changes during the transformations. Whereas phase I has been detected by x-ray diffraction<sup>4,5</sup>, differential thermal analysis<sup>8,47</sup> and dilatometry<sup>2,13</sup> the same has not been confirmed by electrical conductivity, and infra-red absorption studies. Differences in conductivity changes, at phase transformation  $\text{II} \rightleftharpoons \text{III}$  and  $\text{III} \rightleftharpoons \text{IV}$ , observed on recycling in  $\text{RbNO}_3$  have remained unexplained. It is, therefore, thought worthwhile to study the whole spectrum of properties in all phases of  $\text{RbNO}_3$  and synthesize the results for a better understanding of the phase transformations in  $\text{RbNO}_3$  and its solid solutions and propose a suitable model for these transformations.

Hence a detailed study of the phase transformations

in  $\text{RbNO}_3$  has been undertaken by means of (ac) electrical conductivity, differential thermal analysis, dilatometry, high temperature X-ray examination and infra-red absorption.

Thermal hysteresis at the transformations and co-existence of phases in the transformation regions are also investigated.

Disordering of the  $\text{NO}_3$  group in various phases is examined.

The study is extended to cover the influence of substitution of  $\text{K}^+$  (ionic radius =  $1.33 \text{ \AA}^0$ ) and  $\text{Cs}^+$  (ionic radius =  $1.68 \text{ \AA}^0$ ) for  $\text{Rb}^+$  (ionic radius =  $1.48 \text{ \AA}^0$ ) in  $\text{RbNO}_3$  on the phase transitions.



## Chapter 3

### EXPERIMENTAL TECHNIQUES

#### 3.1 Sample Preparation:

$\text{RbNO}_3$  and  $\text{CsNO}_3$  were obtained from Penn Rare Metals Inc., Revere, Penna (USA). The purity claimed by the manufacturer is 99.8 and 99.9% respectively.  $\text{KNO}_3$ , of Analar quality, was obtained from the British Drug House.

$\text{RbNO}_3$  in powdered form, as supplied, was the starting material for investigations on  $\text{RbNO}_3$ . Solid solutions were prepared by heating  $\text{RbNO}_3$  with a known molar % of  $\text{CsNO}_3$  or  $\text{KNO}_3$  in a platinum crucible to a temperature of about  $20^\circ\text{C}$  above the melting point of the material. This temperature was maintained constant for half-an-hour to allow for thorough mixing and formation of a solid solution. Homogeneity of the solid solutions was confirmed by X-ray diffraction methods. The solid solutions so formed were crushed to a powder.

DTA and X-ray measurements were made on powdered samples. The powders were melted and poured into a platinum foil tube to make rods of about 1.5 cm length and 4 mm diameter.

for dilatometric measurements. The fine powder was pressed at  $4.22 \times 10^5 \text{ gm} / \text{cm}^2$  pressure into thin 1.2 cm diameter transparent pellets for infra-red work.

### 3.2 Conductivity Measurements

Powdered specimen of  $\text{RbNO}_3$  or its solid solutions was melted in a platinum crucible. A glass cover (fig 3.1) was lowered to dip the platinum foil acting as one of the electrodes, into the melt. The crucible acted as the other electrode. The melt was cooled and was ready for measurements.

This procedure permits a rapid investigation of different compositions. A technique similar to the present one was first employed in the work of Sawada et al<sup>32</sup> for investigating dielectric hysteresis loops of  $\text{KNO}_3$ . Sawada et al note that the complicated arrangement of electrodes does not allow a precise evaluation of the absolute value of the polarization. For the same reason, the conversions of conductance data to the conductivity values, taking into account only the area of the platinum foil electrode and the distance between the foil and the bottom of the crucible, may be correct to  $\pm 10 \%$ .

Using General Radio 1608 A impedance bridge, at a frequency of 1 KC/S, conductance was measured between  $120^\circ\text{C}$  and the melting point during heating and cooling the compositions. Below  $120^\circ\text{C}$  the conductance was too low to be reliably measured on the bridge. The (ac) electrical conductivity was measured to avoid electrolysis of the ionic salt and to avoid the voltages which may be developed due to polarization effects. The temperatures were measured with a chromel-alumel thermocouple and

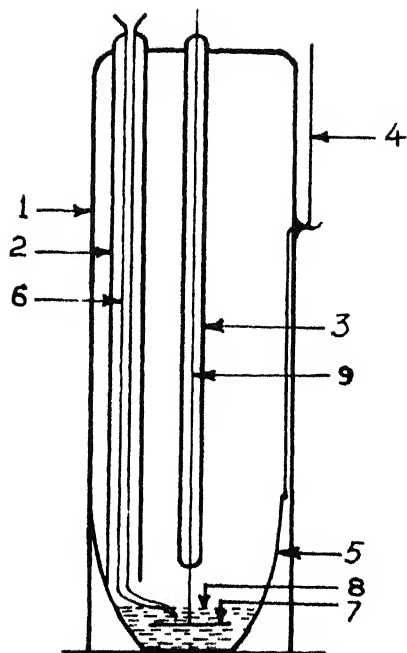


Fig. 3.1 Platinum crucible (5), containing the material (8) under study. Platinum foil (7) and the crucible are acting as the two electrodes. (2) and (3) are glass tubes containing the platinum wire (9), carrying one electrode, and the thermocouple (6). (4) is a lead for the crucible electrode and (1) is the pyrex glass cover.

a Rubicon potentiometer. The rates of heating and cooling during the measurements varied between  $1.5$  to  $2^{\circ}\text{C}$  per minute. The measurements on each specimen were repeated both on heating and cooling and were found reproducible (not shown in the figures). Solid solutions cooled down to a clear solid mass upto 20 mole % of  $\text{CsNO}_3$  in  $\text{RbNO}_3$  while a separate small white patch was observable in the clear cooled mass of solid solutions at 25 molar %  $\text{CsNO}_3$  and above. The cooled solid solutions of  $\text{K}_{1-x}\text{Rb}_x\text{NO}_3$  yielded a clear mass upto 2 molar %  $\text{KNO}_3$  and a white opaque solid at 4 molar % and above.

### 3.3 Differential Thermal Analysis (DTA).

Gordon<sup>62</sup> has described the principle of Differential Thermal Analysis and various DTA instruments including that of the American Instrument Co., which was used in this investigation.

About 0.3 to 0.4 gm of the powder of  $\text{RbNO}_3$  or its solid solutions  $(\text{Cs}, \text{Rb})\text{NO}_3$  and  $(\text{K}, \text{Rb})\text{NO}_3$  was packed into one of the sample holders (a hole) in the metal block of DTA apparatus, the other hole being packed to an equal volume with a reference material - quartz ( $\text{SiO}_2$ ) powder. The furnace was heated at the rate of  $8^{\circ}\text{C}/\text{min}$ . On reaching the maximum temperature the furnace was put off and it was allowed to cool at a natural rate. For recording the differential thermogram a sensitivity of temperature differential of  $0.1^{\circ}\text{C}$  per inch of the chart paper was employed. The maximum temperature to which each sample was heated was about  $40^{\circ}\text{C}$  below the melting point so that the  $\text{II} \rightleftharpoons \text{I}$  transformation

in  $\text{RbNO}_3$  and its solid solutions was not recorded (since it was too close to the melting point).

Temperatures near the melting point of  $\text{RbNO}_3$  were avoided to guard against the corrosive tendency of molten  $\text{RbNO}_3$  for the Inconel sheath of the chromel alumel thermocouple used in the sample holder.

### 3.4 Dilatometric Measurement of Thermal Expansion

The thermal expansion of rod specimens, of  $\text{RbNO}_3$  and its solid solutions, of diameter 4 mm and length 1.5 cm was measured using a fused-quartz tube dilatometer with an optical lever having a magnification of about 450 (Appendix C). The measurements were performed both on heating and cooling, the rate of temperature change being  $2^\circ\text{C} / \text{min}$ . The measurements were continued upto a temperature of about  $20^\circ\text{C}$  below the melting point. Beyond that temperature the sample rod begins to deform plastically.

### 3.5 X-Ray Diffraction Study.

X-ray diffraction methods were used for (i) establishing solid solution formation, (ii) lattice parameter study as a function of temperature, (iii) thermal hysteresis in transformation regions, and (iv) Co-existence of phases in the transformation range

#### 3.5.1 Room Temperature Study.

Solid solution compositions in the systems  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  and  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$ , cooled from the liquid state, were examined at room temperature, using  $\text{CuK}\alpha$  radiation. General Electric XRD-6 diffractometer and a GEXRD-5 x-ray unit with a 11.4 cm

diameter Debye-Scherrer Camera were used for this study.

Reflections with  $2\theta \leq 60^\circ$  were employed for lattice parameter determinations.

### 3.5.2 Lattice Parameters

Powder diffractometer traces of  $\text{RbNO}_3$  and its solid solutions  $(\text{Cs}, \text{Rb})\text{NO}_3$  and  $(\text{K}, \text{Rb})\text{NO}_3$  were recorded as a function of temperature using Tempress Research furnace with a controller on the General Electric XRD-6 x-ray diffraction unit. The powder sample was packed into a rectangular depression of the platinum sample holder which was inserted in its place in the furnace. Slits used were  $1^\circ$  collimator slit, medium resolution soller slit, and  $0.02^\circ$  detector slit. Scanning rate was  $0.2^\circ$  ( $2\theta$ ) per minute and recording was at 12 " (or 30.48 cm) per hour [i.e.  $1^\circ$  ( $2\theta$ ) per inch of chart paper]. Temperature was maintained constant within  $\pm 2^\circ \text{C}$  for half-an-hour or more before recording the diffraction pattern.

$\text{CuK}\alpha$  radiation was used. Lattice parameters were calculated from reflections in the range  $20^\circ < 2\theta < 60^\circ$ . Maximum error in the measurement of d values is therefore  $\pm 0.055\%$ .

### 3.5.3 Thermal Hysteresis

Thermal hysteresis at the transformation region was studied by two methods : dynamic and static methods.

The dynamic method described below is similar to the one employed in the work of Wahl et al.<sup>63</sup> and Schneer and Whiting<sup>64</sup>. In this method an angular range of  $2\theta = 2^\circ$  was continuously scanned around the line (110) by oscillating the diffractometer over this range during heating and around (102)

during cooling. During heating (110) vanishes in  $\text{III} \rightarrow \text{II}$  transformation whereas (102) vanishes in the reverse transformation. While the diffractometer was oscillating to trace the same diffraction line the temperature was recorded as a function of time on a Moseley X-Y recorder. The heating rate was  $1^\circ\text{C}/\text{Min}$  and the scanning rate was  $4^\circ(2\theta)/\text{Min}$ . Time-temperature and  $2\theta$ -time graphs were utilized to find the  $2\theta$  vs temperature record. Height of the x-ray line during heating and cooling was plotted as a function of temperature (Fig 5.4). In the static method, the temperature was kept constant and the (110) as well as the (102) lines were recorded at each constant temperature while traversing the transformation region, continuing till (110) vanishes during heating [(102) appears before (110) vanishes] and until (102) vanishes during cooling [(110) appears before (102) vanishes]. A plot of peak height vs temperature during heating and cooling yields a hysteresis loop (Fig 5.5).

#### 3.5.4 Coexistence of Phases.

Diffraction lines (110), characteristic of phase III, and (102), characteristic of phase II, are recorded at each constant temperature in the static method. Appearance of phase II before III vanishes and vice versa is seen through the trace of these lines (Fig 5.2)

#### 3.6 Infrared Absorption

Thin transparent pellets of  $\text{RbNO}_3$  and its solid solutions, prepared in the manner described in section 3.1, were placed between two asbestos paper rings and supported in a

pyrex glass holder (fig 3.2). The pyrex glass holder consists of two glass tubes sliding into each other. The diameter of the outer tube was reduced at one end so that the inner tube cannot pass through this end. The glass holder was placed inside in a pyrex glass double walled infrared cell (fig 3.2) containing a cylindrical furnace. The cell was mounted on the window of the infra-red spectrophotometer. This high temperature infrared cell is constructed following Vranty and Graves<sup>65</sup>. While the furnace was heated, the outside was cooled by forcing air through the double-wall. The temperature was maintained constant within  $\pm 2^{\circ}\text{C}$  by an Electromax temperature controller and measured by a chromel-alumel thermocouple kept close to the sample. The spectra were recorded on a Perkin-Elmer model 521, double beam Grating-infra-red Spectrophotometer.

Figs 4.18 and 4.19 show the spectra of the transparent pellets of  $\text{RbNO}_3$  at different temperatures marked thereon and the figs 4.18 and 4.19 that of the solid solutions  $\text{Cs}_{0.10}\text{Rb}_{0.90}\text{NO}_3$  and  $\text{K}_{0.02}\text{Rb}_{0.98}\text{NO}_3$  at room temperature.



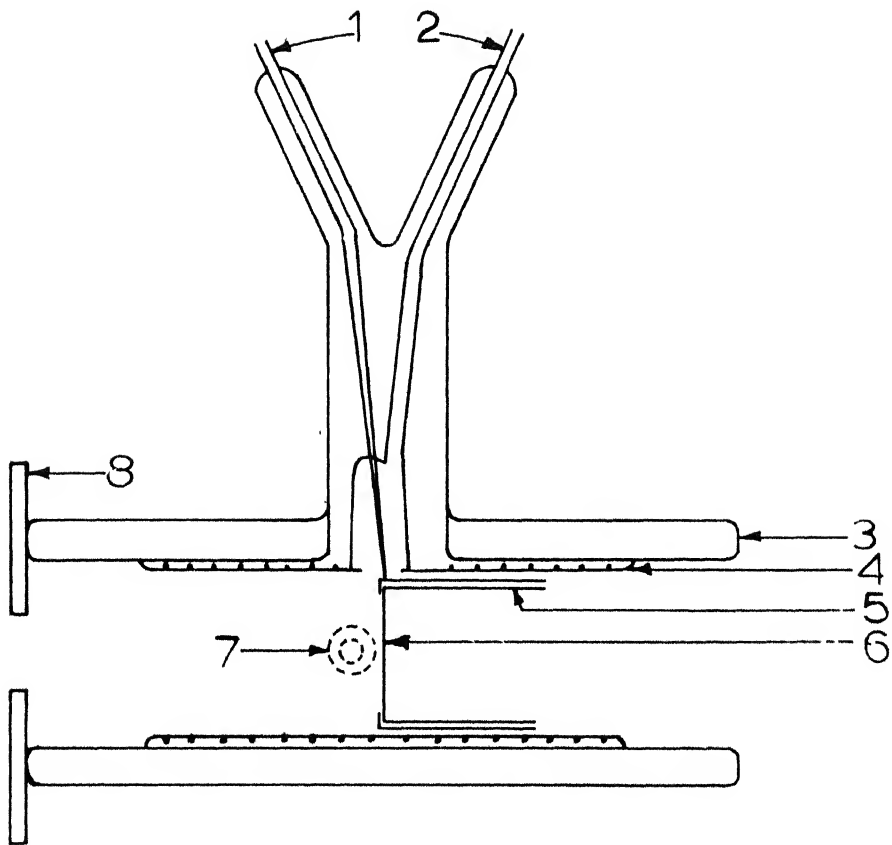


Fig. 3.2 High temperature infrared cell. (1) Chromel-alumel thermocouple, (2) heater leads, (3) double-walled pyrex glass cylinder, (4) Nichrome wire wound (pyrex glass muffle) furnace, (5) Pyrex glass sample holder, (6) sample (pellet), (7) inlet and outlet to double-walled cylinder for air cooling and (8) a brass strip to hold the cell onto the infrared spectrophotometer window.

## Chapter 4

### RESULTS

#### 4.1 Electrical Conductivity

##### 4.1.1 Rubidium Nitrate

A plot of conductivity of  $\text{RbNO}_3$  vs  $1000/T$  ( $T$  is the absolute temperature), on a semi-log scale, in the temperature range  $120^\circ\text{C}$  to above the melting point, is shown as the lower most curve of figs. 4.1 and 4.2<sup>(also Appendix D)</sup>. It is evident from this curve, as pointed out by Brown and McLaren<sup>4</sup>, that phase transformations in  $\text{RbNO}_3$  are marked by discontinuities in electrical conductivity. The magnitude and the nature of the conductivity changes at the phase transitions are tabulated below.

Transition	Conductivity change
IV $\rightarrow$ III	Sudden increase by a factor of about 1000 (corresponding decrease during the reverse transformation)
III $\rightarrow$ II	Sudden drop by a factor of about 100 (corresponding increase during cooling).
II $\rightarrow$ I	Gradual increase by a factor of about 3 (gradual decrease by a factor of about 25 in the reverse transformation)
I $\rightarrow$ Liquid	Gradual increase by a factor of about 200 (gradual decrease by a factor of 35 during cooling).

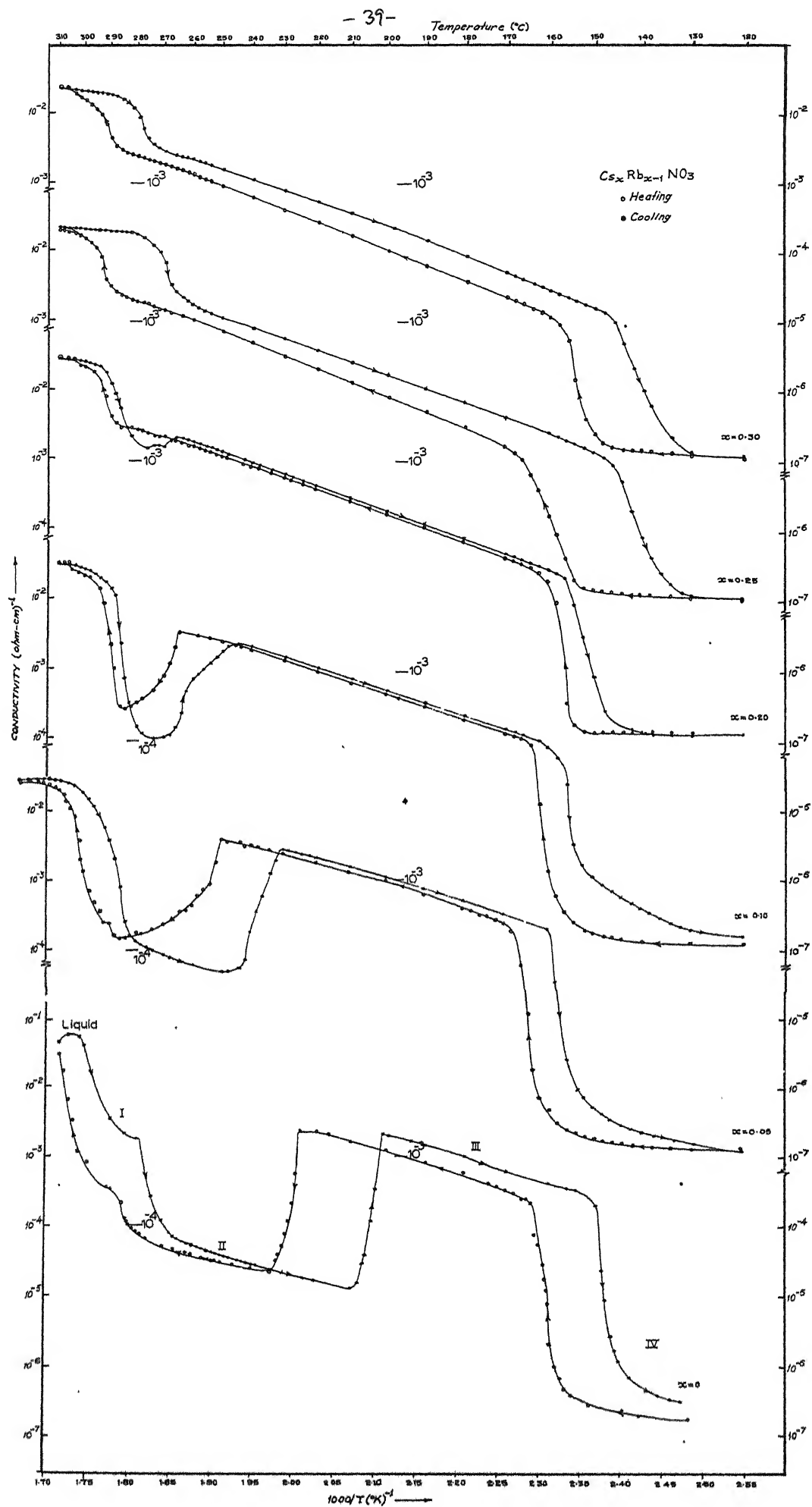


Fig. 4.1: Temperature dependence of electrical conductivity in the system  $Cs_xRb_{1-x}NO_3$

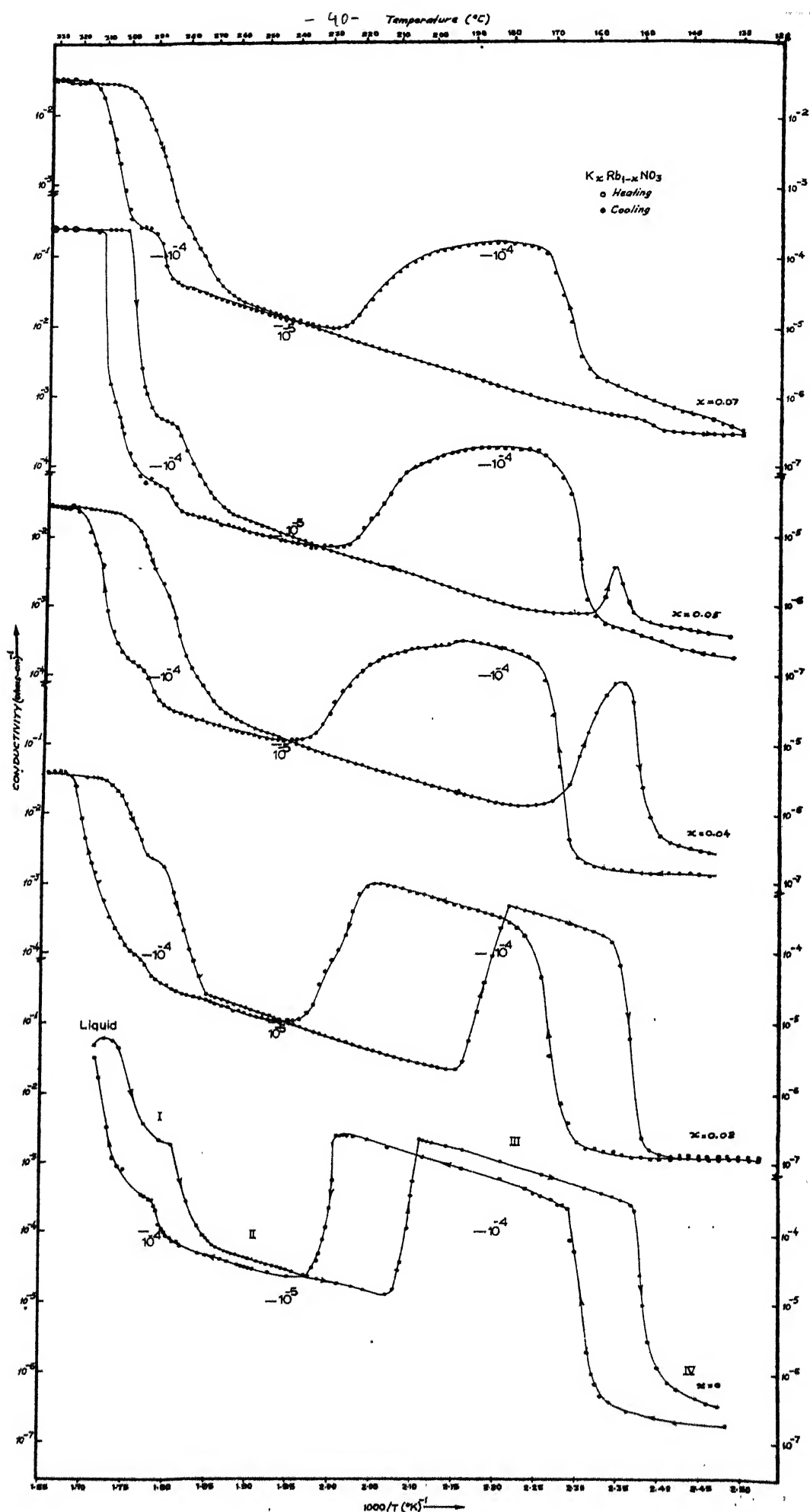


Fig. 4.2: Temperature dependence of electrical conductivity in the system  $K_x Rb_{1-x} NO_3$ .

The magnitude of the conductivity changes observed at  $II \rightarrow I$  and  $I \rightarrow II$  as also at  $I \rightarrow \text{liquid}$  and  $\text{liquid} \rightarrow I$  are markedly unequal. This is probably due to the gradual nature of these transitions. It is, therefore, expected that the magnitude of the steps observed in conductivity plots would be a function of the rate of temperature change. The orders of magnitude of conductivity changes observed here are in good agreement with those reported by Brown and McLaren<sup>4</sup> (fig. 1.4) except during the first cycling. These data confirm the observations of Brown and McLaren<sup>4</sup> that the higher symmetry (cubic) phases (I and III) have high electrical conductivity and low symmetry phases (trigonal IV and hexagonal II) have low conductivity.

The conductivity curve for  $RbNO_3$  also shows that for each stable phase a plot of  $\log \sigma$  vs  $1/T$  yields a straight line. This follows from the relation between the conductivity of a solid and its absolute temperature,  $T$ , i.e.

$$\sigma = A e^{-E/kT}$$

$$\text{or } \log \sigma = \log A - E/kT$$

where  $A$  is a constant,  $E$  is the activation energy for conduction and  $k$  is the Boltzmann constant. From the slopes of these straight lines the activation energies of different phases of

$\text{RbNO}_3$  are calculated and are given below (table 4.1).

Table 4.1 Activation energy for electrical conduction for different phases of  $\text{RbNO}_3$

Phase	Activation Energy E (ev)	
	during heating	during cooling
II	0.92	0.64
III	0.40	0.30
IV	0.88	1.03

Although no activation energy values are given by Brown and McLaren<sup>4</sup> a comparison, of the relative slopes of the straight line portions (fig 1.4) in different phases of  $\text{RbNO}_3$ , shows that the values of activation energy for the three different phases as tabulated here are of the correct relative order. It is clear from table 4.1 that the high symmetry phase (i.e. phase III) has a lower activation energy as compared to low symmetry phases (phases IV and II), as expected. Also out of the low symmetry phases, the one at lower temperature (phase IV) has a higher activation energy as compared to that at higher temperature (phase II). This is again an expected result.

The phase transformation temperatures during heating and cooling, observed from the conductivity plot for  $\text{RbNO}_3$ , are shown in table 4.2. The difference between these temperatures gives the temperature hysteresis at these transformations.

The transition temperatures found by the various methods of study are in reasonable agreement with each other and with those in literature. The temperature hysteresis at the III  $\rightarrow$  II transition found by static x-ray method agrees well with that reported by Calorimetric method<sup>44</sup>. Other methods of study give larger temperature hysteresis. This is probably due to relatively faster rates of heating and cooling. In this connection it may be noted that the fastest rates of heating and cooling are employed in the DTA study.

#### 4.1.2 Solid Solutions in Systems $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$ and $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$ .

In figs. 4.1 and 4.2 are plotted, on a semi-log scale, the conductivity vs reciprocal absolute temperature for  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  and  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  systems respectively. <sup>(Appendix D)</sup> Data obtained during heating and cooling are shown. The phase transition temperatures in these systems, during heating in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system and during heating and cooling in  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system, are summarised in <sup>(also table 4.2)</sup> figs. 4.3 and 4.4 respectively. The general features of the phase diagram, Fig. 4.3, are reproduced by the conductivity data on cooling (not shown in the figure).

TABLE 4.2: Phase transformation temperatures during heating and cooling.

System	Value of x	Transition temperature ( $^{\circ}\text{C}$ )									
		DTA		Conductivity		Dilatometri		X-ray		Other methods	
		h	c	h	c	h	c	h	c	h	c
$\text{bNbO}_3$	x=0	170	159	159	145	158	149			161 <sup>+2</sup>	(2)
		164 <sup>(8)</sup>		164 <sup>(4)</sup>	161 <sup>(4)</sup>			164 <sup>(17)</sup>		160 <sup>(4)</sup>	
		166 <sup>(47)</sup>	153 <sup>(47)</sup>							160 <sup>(44)</sup>	
										164.4 <sup>(45)</sup>	
										161 <sup>(61)</sup>	
$\text{xRb}_{1-x}\text{NbO}_3$	x=0.05	168	155	162	155	158	148			174 <sup>(61)</sup>	
	x=0.10	166	152	158	154	154	144			167 <sup>(61)</sup>	
	x=0.20	152	140	156	148	145	132			161 <sup>(61)</sup>	
$\text{xRb}_{1-x}\text{NbO}_3$	x=0.02	170	158	167	151	156	147				
	x=0.04	163	153	166	147	155					
$\text{bNbO}_3$	x=0	231	213	229	206	216	198	236 <sup>d</sup>	224 <sup>d</sup>		
		219 <sup>(8)</sup>		230 <sup>(4)</sup>	218 <sup>(4)</sup>			231 <sup>s</sup>	223 <sup>s</sup>	219 <sup>+2</sup>	(2)
		228 <sup>(47)</sup>	202 <sup>(47)</sup>							220 <sup>(4)</sup>	
										219 <sup>(5)</sup>	
										199.8 <sup>(26)</sup>	
										218 <sup>(44)</sup>	211 <sup>(44)</sup>
										220 <sup>(45)</sup>	
										217 <sup>(61)</sup>	
$\text{xRb}_{1-x}\text{NbO}_3$	x=0.05	250	230	252	237	240	220	250 <sup>d</sup>	240 <sup>d</sup>	245 <sup>(61)</sup>	
	x=0.10	267	244	274	257	258	240	271 <sup>d</sup>	262 <sup>d</sup>	261 <sup>(61)</sup>	
	x=0.20			283	269					278 <sup>(61)</sup>	
$\text{RbNbO}_3$	x=0.02	218	196	225	185	208	178	223 <sup>d</sup>	199 <sup>d</sup>		
	x=0.04	204		214	164	190		206 <sup>s</sup>	190 <sup>s</sup>		



T/BIF 4.2 (Continued)

System	Value of x	Transition temperature (°C)							
		DTA		Conductivity		Pilotometric		X-ray	
		h	c	h	c	h	c	h	c
$RbNO_3$	$x=0$			284	274	269	263		
		291 <sup>(8)</sup>		282 <sup>(4)</sup>					282 <sup>+1</sup> <sup>(2)</sup>
		278 <sup>(47)</sup>	270 <sup>(47)</sup>						290 <sup>(4)</sup>
									284 <sup>(5)</sup>
									281 <sup>(44)</sup>
$Cs_xRb_{1-x}NO_3$	x=0.05			288	270	264	251		
	x=0.10			292	281				
	x=0.20			292	285				
$K_xRb_{1-x}NO_3$	x=0.02			274	263				
	x=0.04	277	274						

Symbols: h and c represent heating and cooling, d and s stand for dynamic and static methods of X-ray investigations. Numbers in parenthesis indicate reference numbers. DTA temperatures of the present study and of reference 47 refer to the temperatures of the peak of the DTA curves. Values of ref. 61 are obtained from the phase diagram of  $Cs_xRb_{1-x}NO_3$  (figure 1.9).

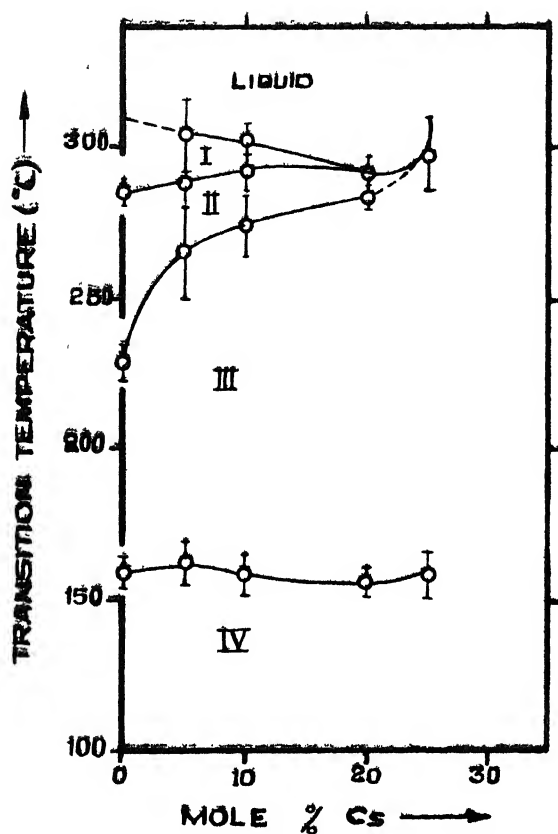


Fig. 4.3 Phase transitions in the system  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$ , based on electrical conductivity data during heating.

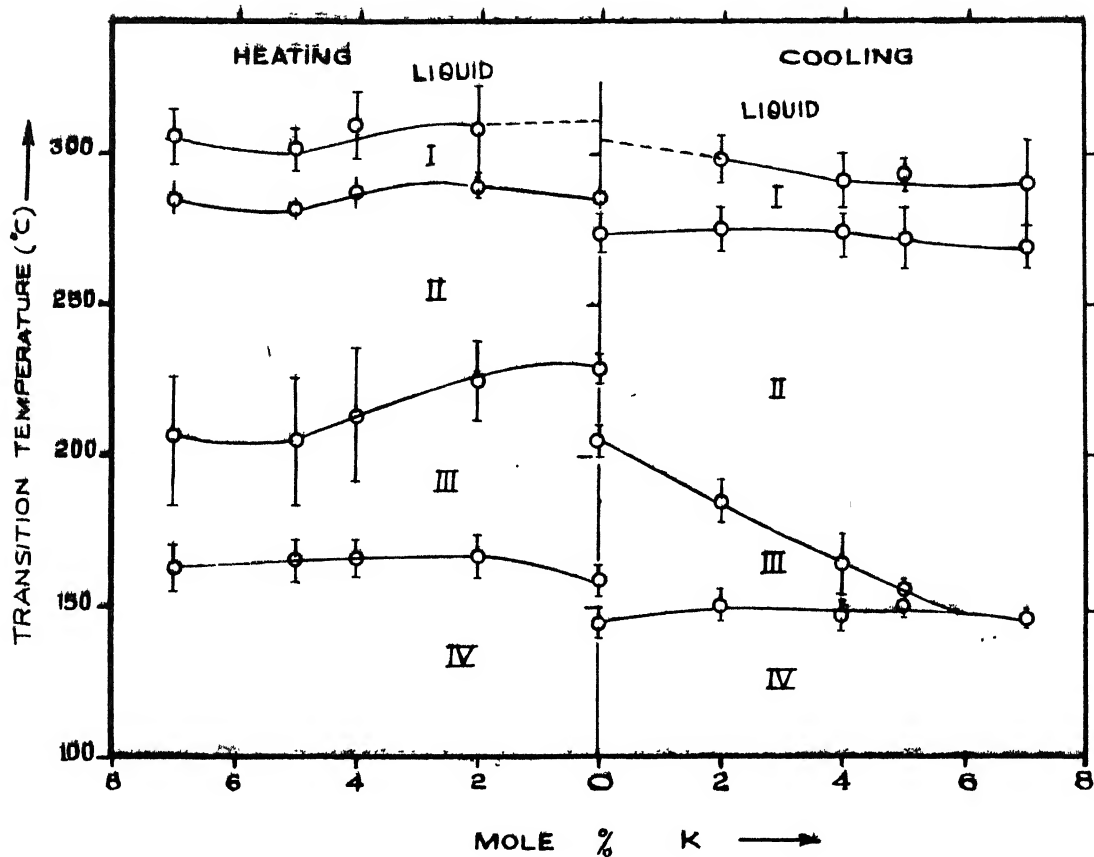


Fig. 4.4 Phase transitions in the system  $K_xRb_{1-x}NO_3$ , based on electrical conductivity data during heating (left) and cooling (right).

The symbols I, II, III, IV and 'liquid' in these diagrams denote the different phases of  $\text{RbNO}_3$  as described in section 1.2. The temperature range of transformation is indicated by the length of the vertical line at each point on these curves (figs 4.3 and 4.4). The effect, of substitution of  $\text{Cs}^+$  or  $\text{K}^+$  for  $\text{Rb}^+$  in  $\text{RbNO}_3$ , on the discontinuities in conductivity, conductivity of different phases and transition temperatures is given below in tabular form (referring to figs. 4.1 and 4.2)

As x increases	$\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$ System	$\text{K}_x\text{Rb}_{1-x}\text{NO}_3$ System
(i) Transition temperature $\text{II} \rightleftharpoons \text{III}$	Decreases slightly	Shifts slightly to lower temperatures
(ii) Transition temperature $\text{III} \rightleftharpoons \text{II}$	Marked shifts to higher temperatures - slightly more during cooling than during heating	Shift to lower temperatures is small during heating and very large during cooling
(iii) Discontinuity $\text{III} \rightleftharpoons \text{II}$	(a) Becomes increasingly sluggish  (b) Disappears between 20 and 25 mole % of $\text{CsNO}_3$	(a) Grows extremely sluggish - largely during heating only  (b) Disappears during cooling at a little above 5 mole % $\text{KNO}_3$ . Does not vanish during heating
(iv) Transition temperature $\text{II} \rightleftharpoons \text{I}$	Shifts slightly to low temperature side	Moves slightly to lower temperatures
(v) Discontinuity $\text{II} \rightleftharpoons \text{I}$	Vanishes at 10 mole % $\text{CsNO}_3$	Continues throughout the range of solid solutions studied

During heating it seems to fade at  $\sim 2$  mole %  $\text{KNO}_3$  but becomes prominent at higher concentrations. During cooling fading is seen at  $\sim 4$  mole %  $\text{KNO}_3$

(vi) Mixing limit	(a) Between 20 and 25 mole % $\text{CsNO}_3$ for phase II. (b) Probably 10 mole % $\text{CsNO}_3$ for phase I.	A little above 5 mole % $\text{KNO}_3$ for phase III (from conductivity data during cooling)
(vii) Melting point	Decreases slightly till the mixing limit after which it appears to increase	Is lowered slightly till the mixing limit after which it seems to rise
(viii) Conductivity of (a) phases III and I, and (b) phase II.	(a) Decreases and (b) Increases	Decreases in all these phases

As seen from fig. 4.1, at concentrations greater than or equal to 25 mole %  $\text{CsNO}_3$  in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system, there is a transition directly from phase III to the melting region. The phases III, II and I have all merged with each other. Structurally, the phases IV and III of  $\text{RbNO}_3$  are probably similar to the two crystalline phases of pure  $\text{CsNO}_3$ . Crystallographic<sup>13</sup>, thermodynamic<sup>49</sup> and high pressure data<sup>36,37</sup> also suggest a similar possibility.

It may be noted from the cooling curves of fig. 4.2 that the region of phase II, in  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system, is getting widened very fast with increasing x. This continues to the

point of non-existence of phase III at a little above 5 mole %  $\text{KNO}_3$  which may thus be regarded as the limit of mixing of  $\text{KNO}_3$  in phase III of  $\text{RbNO}_3$ .

These data confirm the following observations of Dantsiger<sup>58</sup> on  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system : (i) the solubility limit during cooling is between 3 - 5 mole %  $\text{KNO}_3$ , (ii)  $\text{III} \rightleftharpoons \text{II}$  transition point shifts to low temperature side and is increasingly smeared out, and (iii)  $\text{IV} \rightarrow \text{III}$  transition does not disappear at all. Also it confirms the observations of Dantsiger<sup>61</sup> in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  : (i) the transition  $\text{III} \rightleftharpoons \text{II}$  shifts to high temperature side, and (ii) the limit of solubility lies at  $x > 0.20$ . The phase diagram of the present study compares well with that of Dantsiger (fig. 1.9) who could draw this diagram only for phases II, III and IV.

#### 4.1.3 Phase I

In the conductivity plots, Phase I which precedes melting was quite clearly observed, delimited by discontinuous changes in conductivity at each end (figs 4.1 and 4.2), in contrast to the conclusions of Brown and McLaren<sup>4</sup> and Dantsiger<sup>26</sup>. Brown and McLaren detected the transition  $\text{II} \rightleftharpoons \text{I}$  in compressed powder pellets of  $\text{RbNO}_3$  as only a change of slope in the graph of  $\log(\text{conductance})$  vs reciprocal of absolute temperature. Dantsiger could not observe phase I in his dielectric

measurements on cooled melts of  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system since according to him the lower boundary of phase I was too close to the melting region. The existence of phase I has been confirmed by other measurements such as x-ray diffraction<sup>4,5</sup> infrared absorption, specific heat<sup>44</sup>, differential thermal analysis<sup>8</sup> and dilatometry<sup>2</sup>.

#### 4.2 Thermodynamic Parameters by Differential Thermal Analysis

The differential thermograms i.e. a plot of  $\Delta T$  (temperature difference between the sample and reference material) vs temperature of reference, obtained both on heating and cooling are shown in fig 4.5 for  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system and in fig 4.6 for  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system. From figs. 4.5 and 4.6 it can be seen that as x increases : (i) Transformation temperature IV  $\Rightarrow$  III is shifting slowly to low temperature side (ii) Transformation temperature III  $\Rightarrow$  II is shifting markedly towards high temperature direction in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system and in the opposite direction in  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system. In the latter system shifts are more pronounced during cooling than during heating. (iii) II  $\Leftarrow$  I is shifting slowly to low temperature side. As seen in section 4.1.2 the transformation III  $\Rightarrow$  II grows sluggish with increasing concentrations of  $\text{CsNO}_3$  and  $\text{KNO}_3$ . It is evident from figs 4.5 and 4.6 that this slow nature of the transformations except for  $x=0.04$  in fig 4.6 is not detected

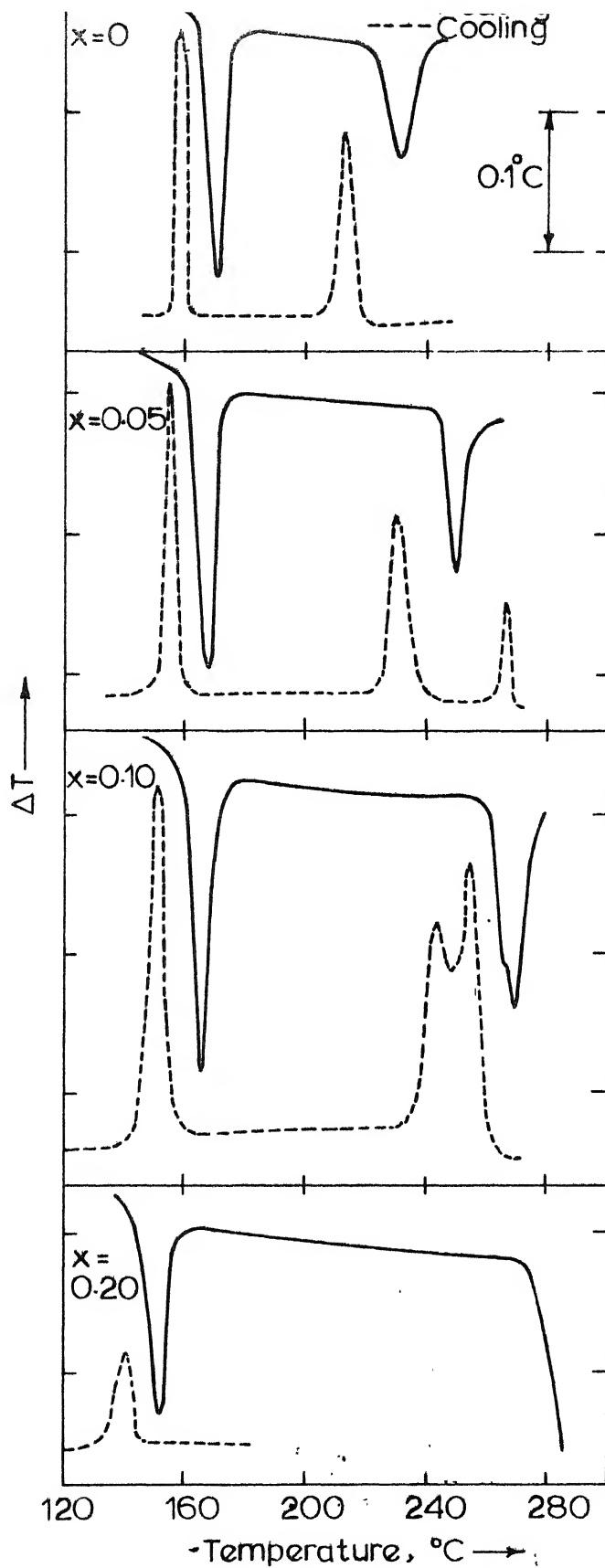


Fig. 4.5 Differential thermograms of  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system.



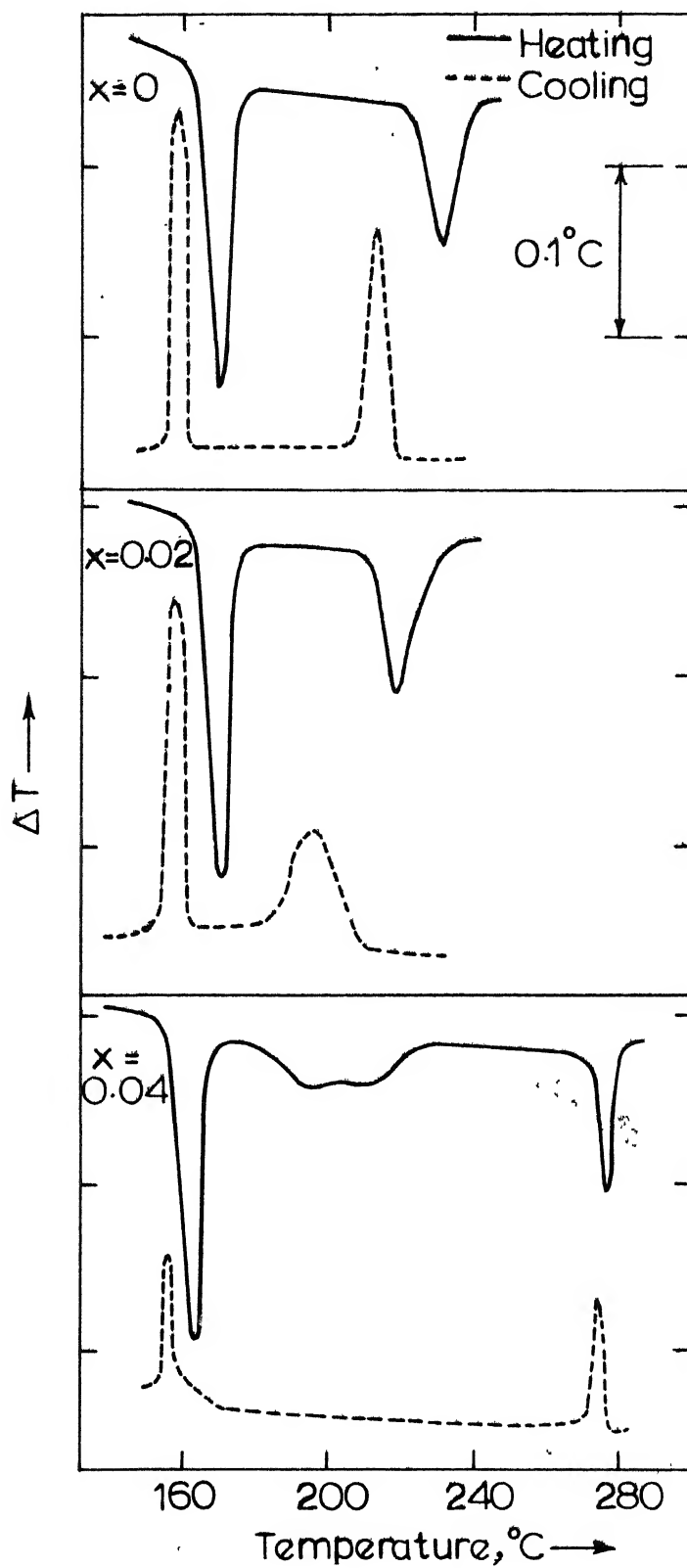


Fig. 4.6 Differential thermograms of  $K_xRb_{1-x}NO_3$  system.

by differential thermal analysis. A somewhat similar conclusion was reached earlier by Rao and Rao<sup>47</sup>. It is also seen from figs 4.5 and 4.6 that transformation  $\text{III} \rightleftharpoons \text{II}$  vanishes at  $x = 0.20$  in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system and  $\text{II} \rightarrow \text{III}$  at  $x = 0.04$  in  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system. These conclusions, from the DTA data, confirm those derived from the conductivity data.

Heats of transition are calculated from the peak areas in DTA curves using the formula (Appendix A)

$$\Delta H = H \frac{m_1}{m_2} \frac{A_2 M_2}{A_1 M_1}$$

where H represents the heat of transformation of a standard material ( $\text{RbNO}_3$  in this case);  $A_1$ ,  $A_2$  are the areas of the respective peaks for standard and sample,  $m_1$ ,  $m_2$  are the masses of the standard & sample materials and  $M_1$ ,  $M_2$  their respective molecular weights. The molecular weights are the weighted mean of the molecular weights of the host and the dopant in the ratio of their composition in the solid solutions. The calculated values for the heats of transition are tabulated (Table 4.3). The value of heat of transition given by Mustajoki<sup>44</sup> (i.e. 932 cal/mole for  $\text{IV} \rightarrow \text{III}$  transformation in  $\text{RbNO}_3$ ) has been assumed for the calculations of  $\Delta H$  for the solid solutions.

Table 4.3 Heats of transitions ( $\Delta H$ ) and thermal energies of activation ( $E_a$ ) from DTA curves.

Material	Transition IV $\xrightarrow{E_a}$ III		Transition III $\xrightarrow{E_a}$ II	
	$\Delta H$ Cal/mole	$E_a$ Kcal/mole	$\Delta H$ Cal/mole	$E_a$ Kcal/mole
Literature values	932 <sup>44</sup> ; 923 <sup>45</sup> ; 950 <sup>47</sup>	165 <sup>47</sup>	767 <sup>44</sup> ; 774 <sup>45</sup> ; 650 <sup>47</sup>	50 <sup>47</sup>
RbNO <sub>3</sub> Present study	-	166	610	104
Cs <sub>0.05</sub> Rb <sub>0.95</sub> NO <sub>3</sub>	1165	110	573	175
Cs <sub>0.10</sub> Rb <sub>0.90</sub> NO <sub>3</sub>	1022	97	372	136
Cs <sub>0.20</sub> Rb <sub>0.80</sub> NO <sub>3</sub>	795	107	-	-
K <sub>0.02</sub> Rb <sub>0.98</sub> NO <sub>3</sub>	1262	108	681	72
K <sub>0.04</sub> Rb <sub>0.96</sub> NO <sub>3</sub>	885	128	717	60

The energy required for a transformation (i.e. the energy of activation  $E_a$ ) can also be calculated from the DTA curves using the method of Borchardt and Daniels<sup>64</sup>. For this purpose the rate constant  $k$  of a reaction given by<sup>64</sup>

$$k = \frac{\Delta T}{A - a}$$

is determined. Here  $A$  represents the total area under the DTA curve (peak), ' $a$ ' and ' $\Delta T$ ' are shown in fig. 4.7. The log  $k$  vs  $1/T$  plots are called the activation energy plots. These are shown in figs 4.8 and 4.9 for IV  $\rightarrow$  III and III  $\rightarrow$  II transformations in RbNO<sub>3</sub>, Cs<sub>x</sub>Rb<sub>1-x</sub>NO<sub>3</sub> and K<sub>x</sub>Rb<sub>1-x</sub>NO<sub>3</sub> systems.

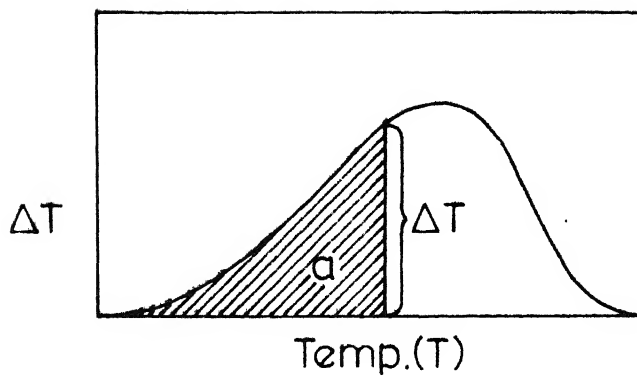


Fig. 4.7 Schematic DTA curve showing the quantities in the rate equation  $k = \Delta T / A - a$  (ref. 64).  $k$  is the rate constant and  $A$  is the area under the curve.

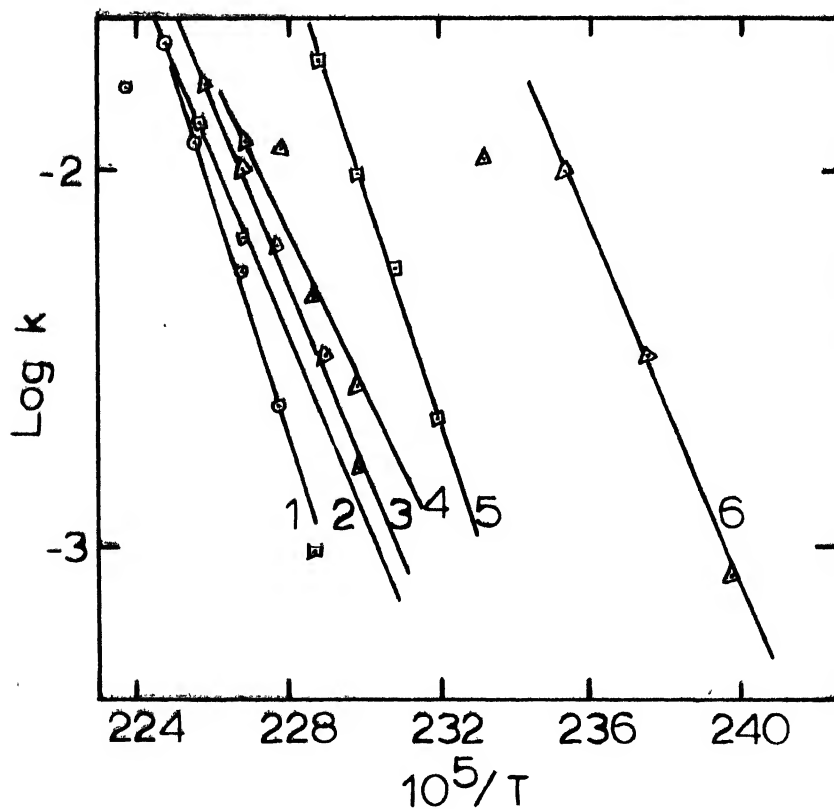


Fig. 4.8 Activation energy plots for IV  $\rightleftharpoons$  III transformation  
Graph '1' is for  $\text{RbNO}_3$ ; 3, 4, 6 for  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$   
( $x = 0.05, 0.10, 0.20$ ) and 2, 5 for  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$   
( $x = 0.02, 0.04$ ).

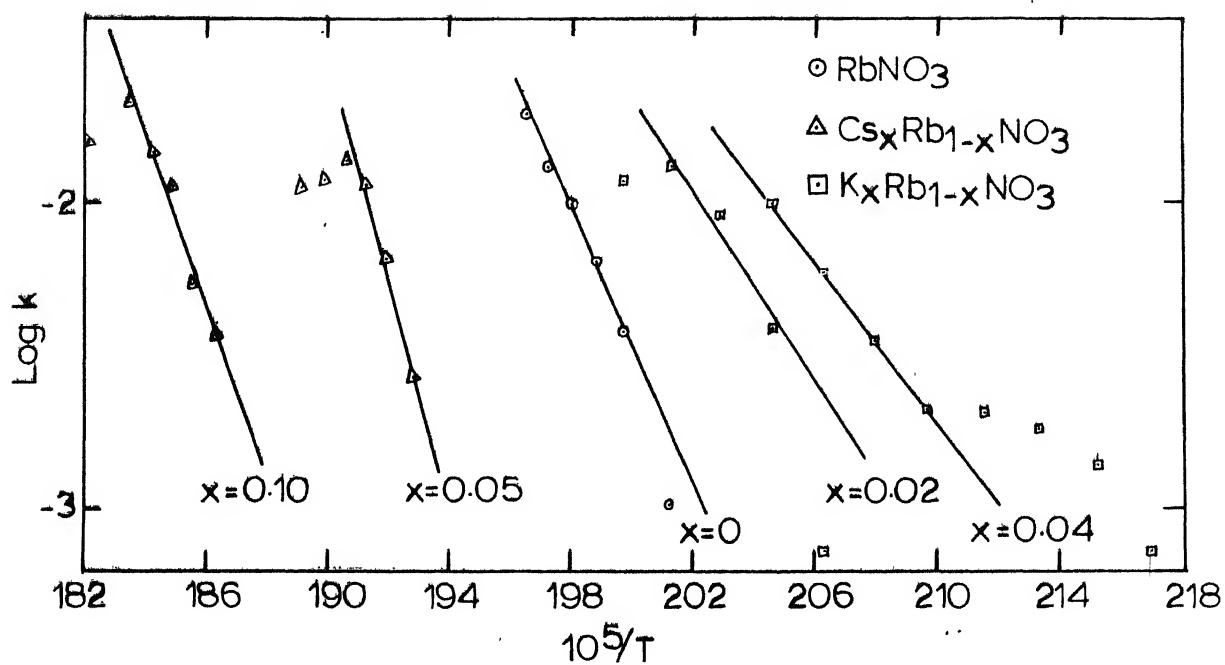


Fig. 4.9 Activation energy plots for  $\text{III} \rightleftharpoons \text{II}$  transformation.

From the slope of these straight line plots\*  $E_a$  is calculated using the formula (Appendix B)

$$E_a = 2.303 R \times (\text{slope of activation energy plot}).$$

where R is the gas constant.  $E_a$  values thus obtained are listed in table 4 3.

According to Rao and Rao<sup>47</sup> the H and  $E_a$  values obtainable from the DTA study have an uncertainty of  $\pm 15 \%$ . The values of activation energies  $E_a$  for IV  $\rightarrow$  III transformation, and heats of transition  $\Delta H$ , for III  $\rightarrow$  II

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\* According to Rao et al<sup>65</sup> there is a considerable controversy regarding the evaluation of k, the first order rate constant, and  $E_a$  from the DTA curves. Inspite of the controversy it may be reasonable to compare values of  $E_a$  in a related series of systems. Further, obtaining good linear plots of  $\log k$  vs  $1/T$  serves as a satisfactory criterion for obtaining meaningful values of  $E_a$ <sup>47</sup>.

transformation in the case of  $\text{RbNO}_3$  are in reasonable agreement with those of Rao and Rao<sup>47</sup> (Section 1.6). The activation energy value for  $\text{III} \rightarrow \text{II}$  transformation in  $\text{RbNO}_3$  as determined here, does not agree with that of Rao and Rao<sup>47</sup>. The larger value for activation energy observed here is consistent with the reconstructive nature of transition at  $\text{III} \rightarrow \text{II}$ , as reported by Kennedy<sup>5</sup>.

The value of  $\Delta H$  at the  $\text{IV} \rightleftharpoons \text{III}$  transition seems to decrease with solid solution formation. It may be recalled that this transition temperature is affected only slightly by ionic substitution. On the other hand, at the  $\text{III} \rightleftharpoons \text{II}$  transition, which is affected markedly by ionic substitution  $\Delta H$  decreases and  $T_a$  increases on replacing  $\text{Rb}^+$  by  $\text{Cs}^+$ . Replacement of  $\text{Rb}^+$  by  $\text{K}^+$  has an opposite effect.

#### 4.3 Thermal Expansion Measurement by a Dilatometer

Figs 4.10 and 4.11 show the plot of  $\frac{\Delta l}{l}$  vs temperature for the  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  and  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  systems. <sup>(Appendix F)</sup> The coefficients of linear thermal expansion (on heating) vs temperature are shown in figs 4.12 and 4.13. From figs 4.10 and 4.11 it can be seen that, (i) the anomalous thermal expansion at

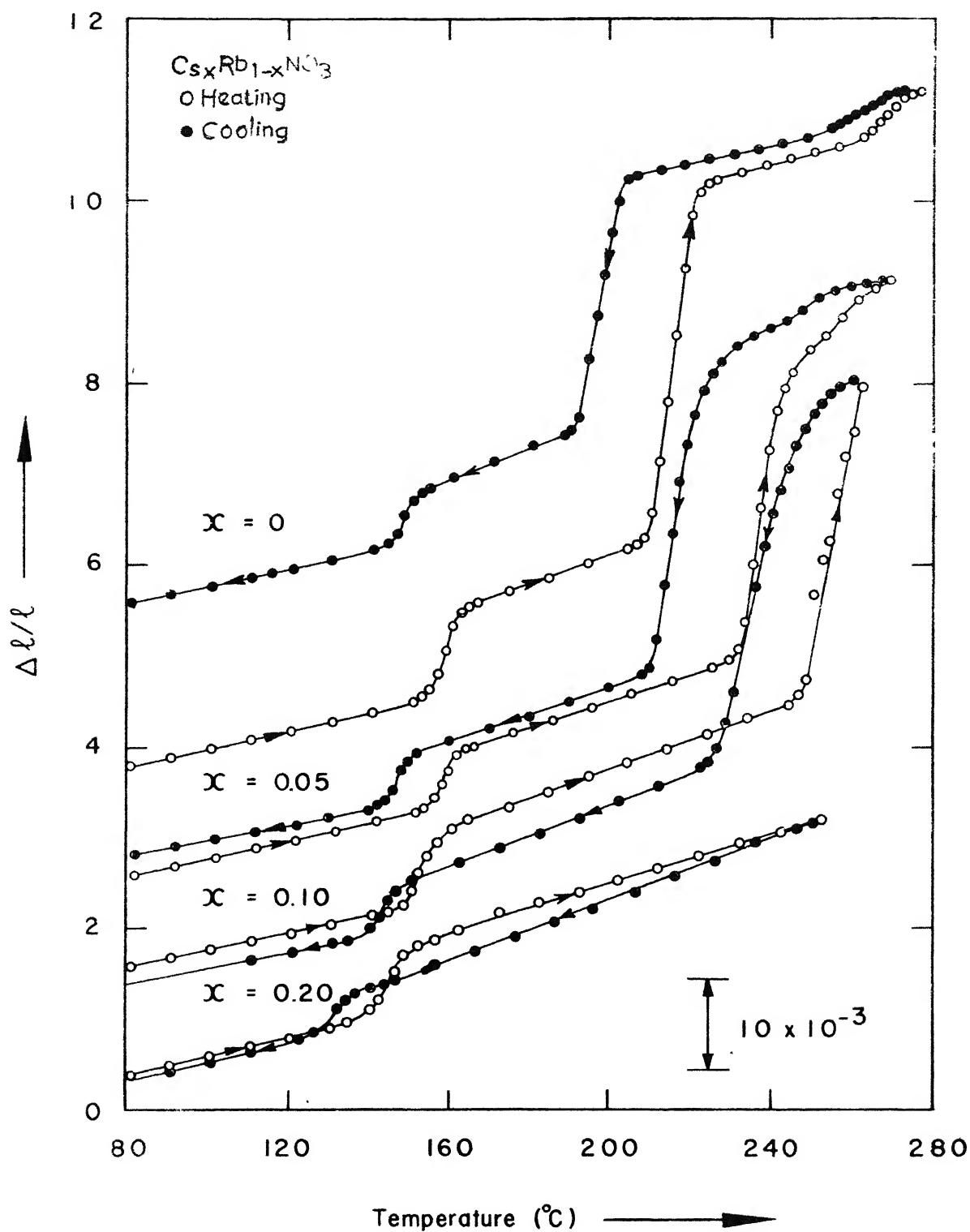


Fig. 4.10 Thermal expansion as a function of temperature for the  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system.



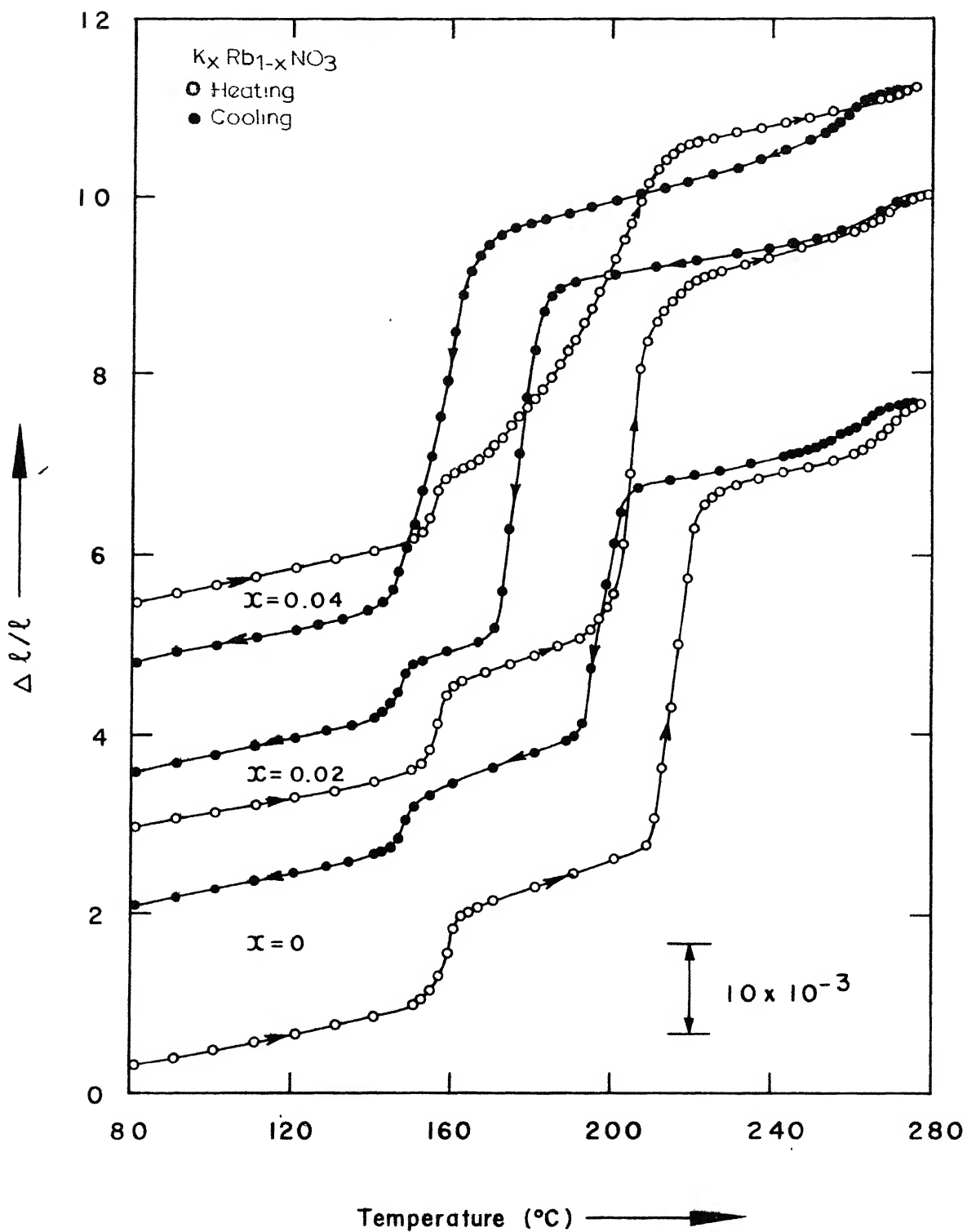


Fig. 4.11 Thermal expansion as a function of temperature for the  $K_x Rb_{1-x} NO_3$  system.

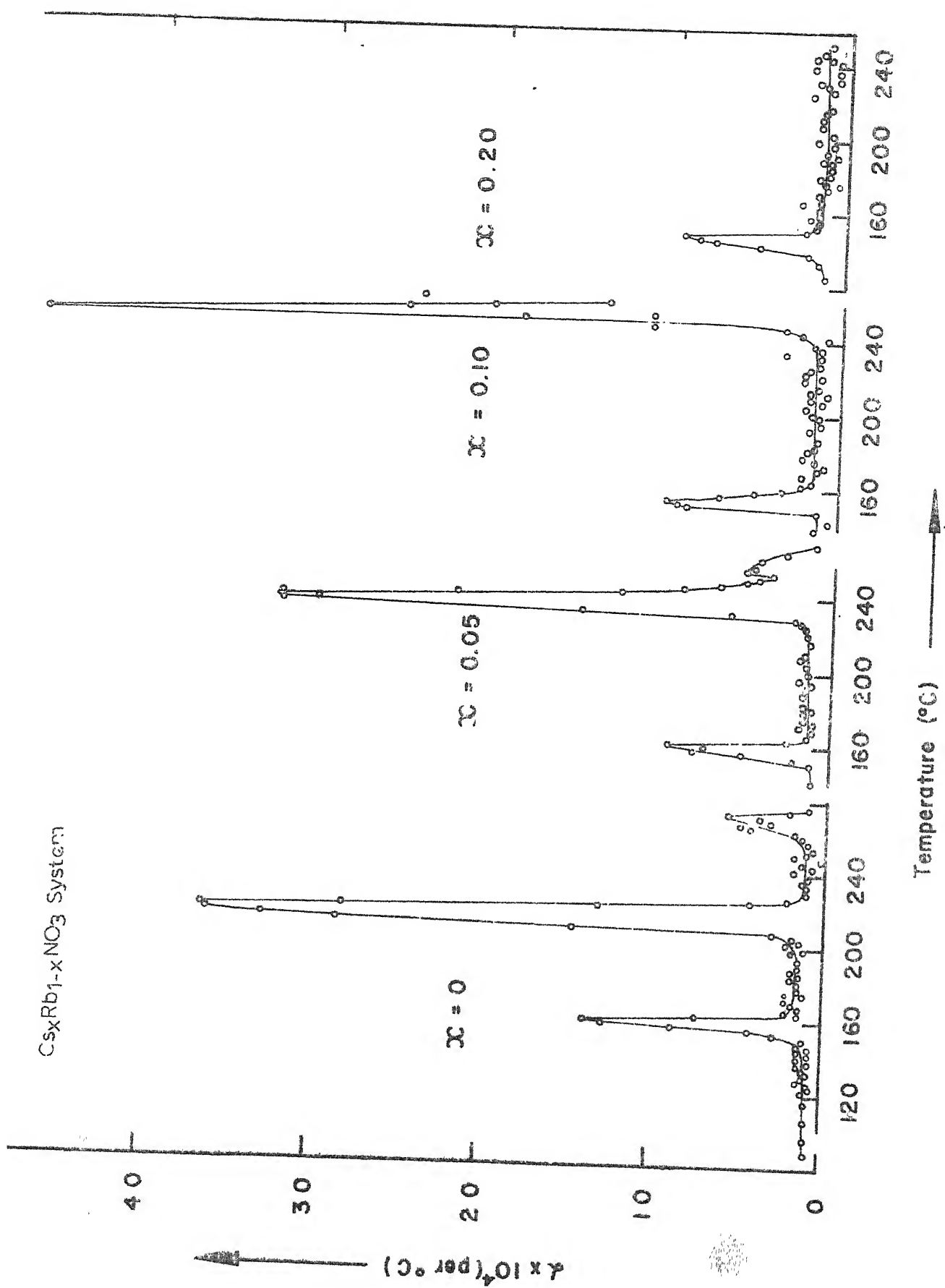
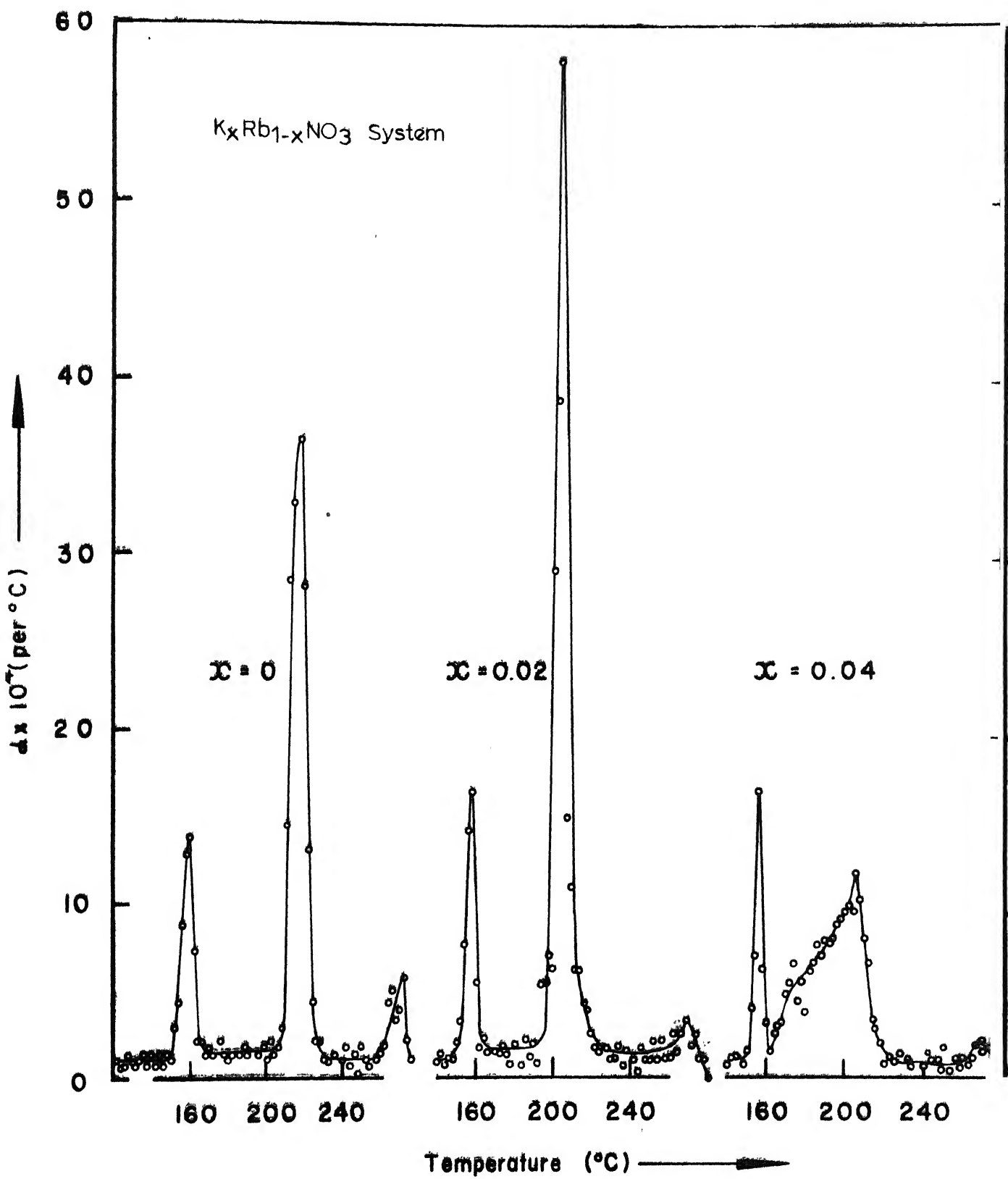


Fig. 4.12: Coefficients of linear thermal expansion as a function of temperature for  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system.



III  $\rightarrow$  II transition is larger than that at the IV  $\rightarrow$  III, which in turn is larger than that at the II  $\rightarrow$  I phase change (table 5.2) (ii) with increasing  $\text{Cs}^+$  or  $\text{K}^+$  concentration, the anomalous expansions, at IV  $\rightarrow$  III and III  $\rightarrow$  II phase changes, decrease during heating and increase during cooling, (iii) IV  $\rightarrow$  III transition temperature decreases slightly with increasing  $\text{Cs}^+$  or  $\text{K}^+$  concentrations, transition temperature III  $\rightleftharpoons$  II shifts substantially to high temperature side in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system and in the opposite direction in  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system, (iv) transition III  $\rightleftharpoons$  II is increasingly getting squeezed out with increasing  $\text{Cs}^+$  or  $\text{K}^+$  concentrations, (v) high temperature end of phase II stays nearly constant in both  $(\text{Cs}, \text{Rb})\text{NO}_3$  and  $(\text{K}, \text{Rb})\text{NO}_3$  systems; its low temperature end shifts with concentration to higher temperatures in  $(\text{Cs}, \text{Rb})\text{NO}_3$  system and in the opposite direction in  $(\text{K}, \text{Rb})\text{NO}_3$  system. Hence in fig 4.10 phase II is getting squeezed out and in fig 4.11 it gets widened. Phase III is gradually vanishing with concentration in  $(\text{K}, \text{Rb})\text{NO}_3$  system — faster during cooling than during heating. It is getting widened in  $(\text{Cs}, \text{Rb})\text{NO}_3$  system with concentration and (vi) the temperature at which the material becomes plastic decreases with concentration of  $\text{Cs}^+$  or  $\text{K}^+$ . It is probably due to the lowering of the melting point.

These conclusions are in conformity with those in sections 4.1 and 4.2.

#### 4.4 Thermal Expansion Study by X-ray Diffraction.

The plots of lattice parameters as a function of temperature in the range 25 - 300°C are shown in figs 4.14 to 4.17 for  $\text{RbNO}_3$  and its solid solutions. <sup>(Appendix G)</sup> The lattice parameter data of  $\text{RbNO}_3$  given in fig 4.14 are replotted in fig 4.15 where the reduced lattice parameters represent one formula unit of  $\text{RbNO}_3$  in each phase. Thus,  $\frac{a_{\text{IV}}}{\sqrt{6}}$  and  $\frac{c_{\text{IV}}}{\sqrt{3}}$  are plotted in place of  $a_{\text{IV}}$  and  $c_{\text{IV}}$ , the hexagonal lattice parameters of phase IV, and  $\frac{a_{\text{II}}}{\sqrt{2}}$  and  $\frac{c_{\text{II}}}{\sqrt{6}}$  in place of the hexagonal parameters  $a_{\text{II}}$  and  $c_{\text{II}}$  of phase II. The interrelationships between the unit cells of different phases are discussed in section 5.1.3.

It can be seen from fig 4.14 that  $c$  and  $a$  in phase IV,  $a$  in phase III and  $c$  in phase II expand with temperature whereas  $a$  in phase II contracts with temperature. Fig 4.15 shows that in phase IV,  $\frac{a_{\text{IV}}}{\sqrt{6}}$  expands while  $\frac{c_{\text{IV}}}{\sqrt{3}}$  contracts near the transformation temperature to become equal to  $a_{\text{III}}$  which expands with temperature.  $a_{\text{III}}$  represents the lattice constant of phase III. In phase II,  $\frac{a_{\text{II}}}{\sqrt{2}}$  contracts with temperature, whereas  $\frac{c_{\text{II}}}{\sqrt{6}}$  expands.

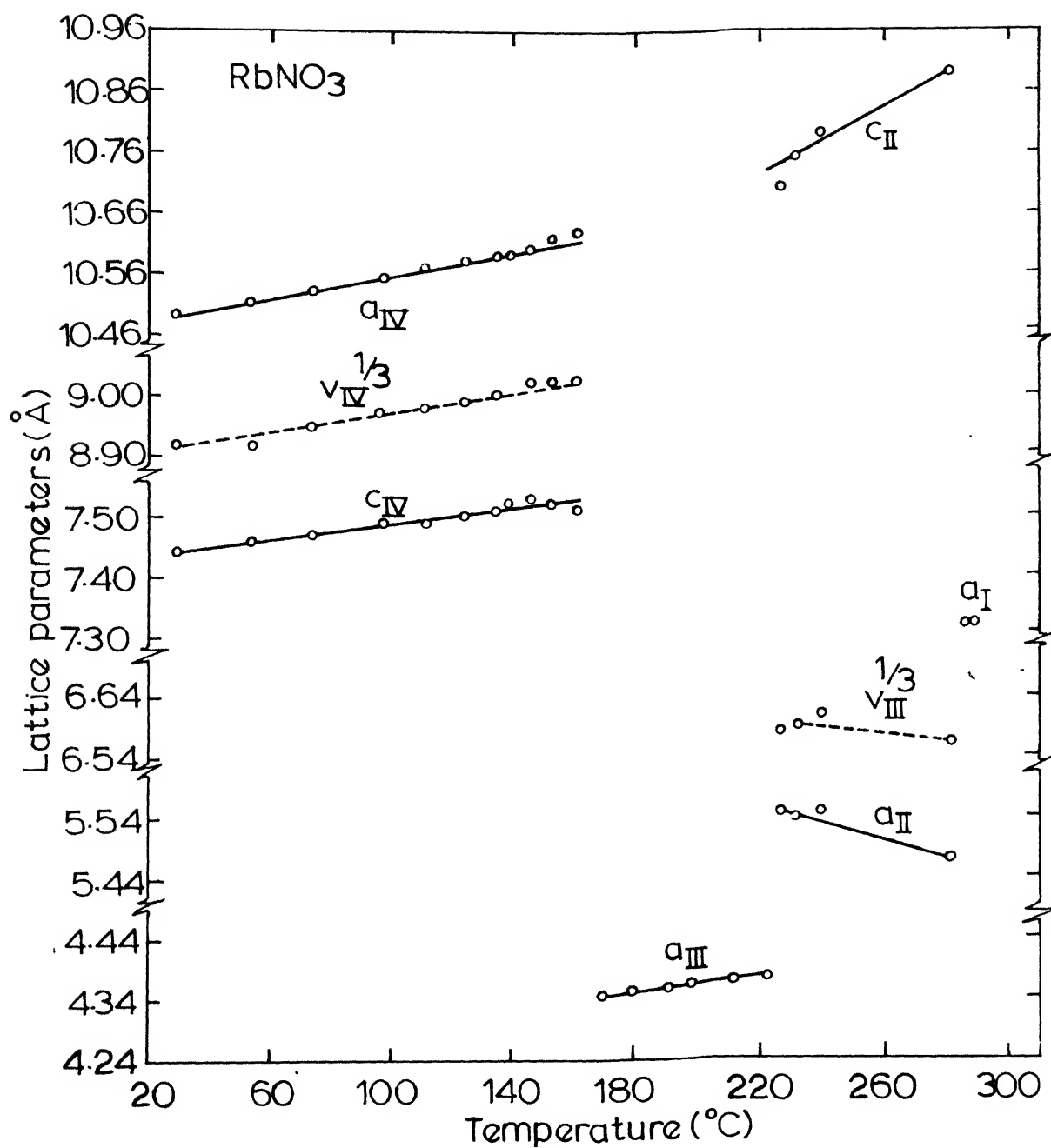
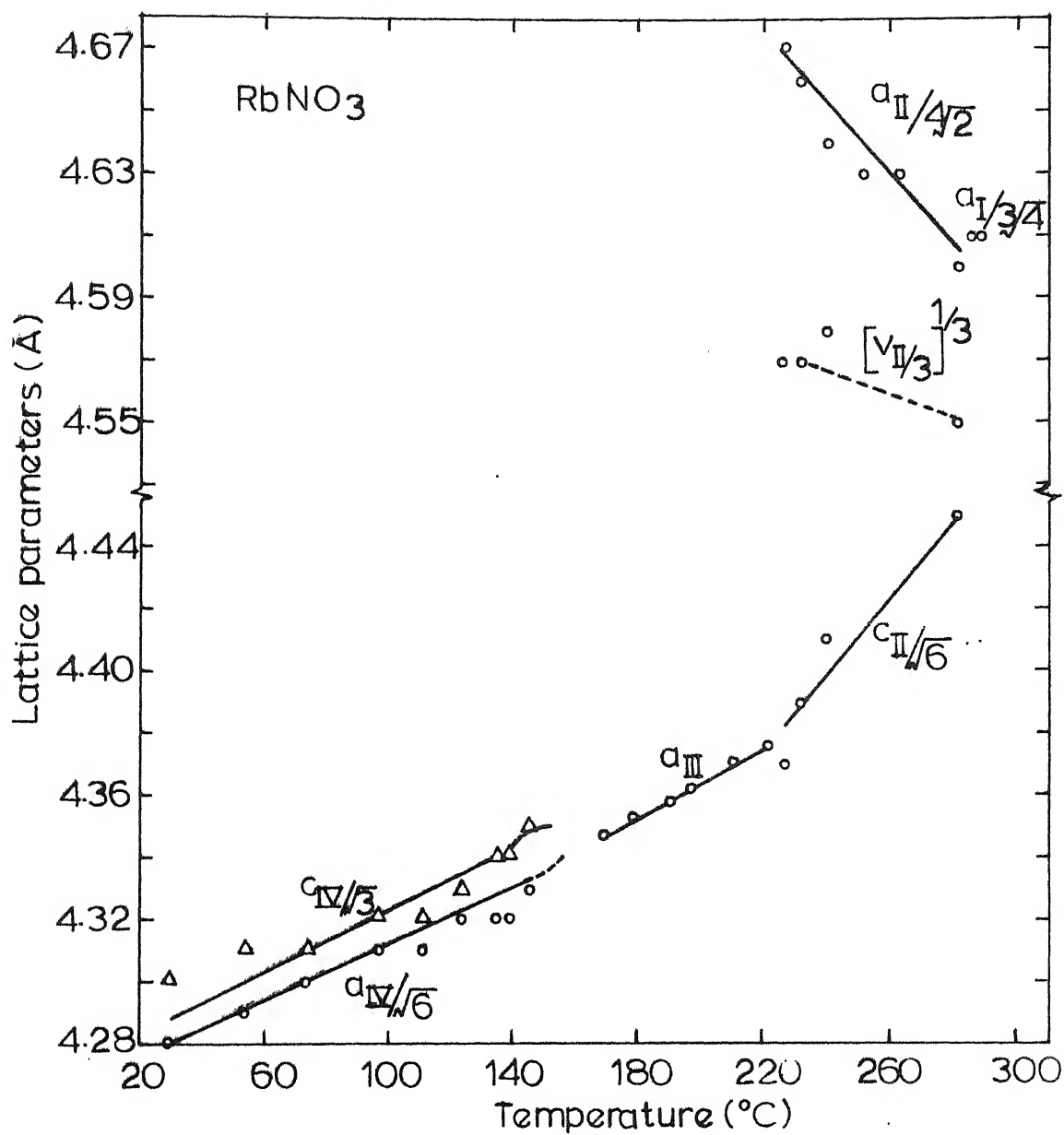


Fig. 4.14: Variation of lattice parameters of the four solid phases of RbNO<sub>3</sub> with temperature.



4.15 Temperature dependence of reduced lattice parameters of RbNO<sub>3</sub>. The lattice parameters of each phase are reduced to include one formula weight of RbNO<sub>3</sub>.

Table 4.4 compares the lattice parameter values of different authors with those found in the present study.

Table 4.4 Lattice parameters of different phases of  $\text{RbNO}_3$  as studied by different authors

Phase	Type of study	Authors	Lattice parameters	No. of formula units per unit cell	Lattice parameters of present study
IV	Single crystal	Brown & McLaren <sup>4</sup>	Trigonal: $a = 10.51 \text{ \AA}$ $c = 7.43 \text{ \AA}$	9	$a = 10.51 \text{ \AA}$ $c = 7.43 \text{ \AA}$
-do-	-do-	Pauling & Sherman <sup>6</sup>	Hexagonal: $a = 10.45 \text{ \AA}$ $c = 7.38 \text{ \AA}$	-do-	
III	-do-	Brown & McLaren <sup>4</sup>	Cubic: $a = 4.36 \text{ \AA}$	1	$a = 4.36 \text{ \AA}^*$
-do-	Powder photograph	U. Korhonen <sup>11</sup>	Cubic $a = 8.74 \text{ \AA}$	4	
II	Powder diffraction	Brown & McLaren <sup>4</sup>	Tetragonal: $a = 6.19 \text{ \AA}$ $c = 8.74 \text{ \AA}$	4	
-do-	-do-	-do-	Hexagonal: $a = 5.48 \text{ \AA}$ $c = 10.71 \text{ \AA}$	3	$a = 5.51 \text{ \AA}$ $c = 10.74 \text{ \AA}$
I	Powder diffraction	Brown & McLaren <sup>4</sup>	Cubic: $a = 7.32 \text{ \AA}$	4	$a = 7.30 \text{ \AA}$

\* This value of lattice constant does not exclude the possibility of the cell of double this size, proposed by Korhonen<sup>11</sup> since the nitrogens and oxygens do not contribute much to the X-ray reflections and hence not identified here.



The variations of reduced lattice parameters with temperature for  $\text{Cs}_{0.05}\text{Rb}_{0.95}\text{NO}_3$  and  $\text{K}_{0.04}\text{Rb}_{0.96}\text{NO}_3$  are shown in figs 4.16 and 4.17 respectively. The data are similar to those recorded for  $\text{RbNO}_3$ . A widening of the temperature range of stability of phase III with the addition of  $\text{Cs}^+$  and a narrowing of this range with the addition of  $\text{K}^+$  is quite apparent from these figures. The lattice parameters are observed to vary non-linearly in the close vicinity of the phase transformations (see e.g. the  $\text{II} \rightarrow \text{I}$  transformation in  $\text{K}_{0.04}\text{Rb}_{0.96}\text{NO}_3$  in fig. 4.17).

The thermal expansion behaviour of phase IV of  $\text{RbNO}_3$  (fig 4.14) is in confirmity with the dilatometric results of Dantsiger and Fesenko<sup>26</sup> (fig 1.6) who find that single crystals of  $\text{RbNO}_3$ , in phase IV, expand both along the trigonal axis as well as in a direction perpendicular to it (section 1.5). However, in contrast to the contraction along both the axes of phase IV at  $\text{IV} \rightarrow \text{III}$  transformation and also in phase III reported by Dantsiger and Fesenko<sup>26</sup>, the present results indicate that one of the axes of phase IV expands and the other contracts at  $\text{IV} \rightarrow \text{III}$  transformation and the unit cell edge expands in phase III. These results confirm those of Kennedy<sup>17</sup> who carried out X-ray diffraction study of single crystals of  $\text{RbNO}_3$ . Due to the disruptive nature of the  $\text{III} \rightarrow \text{II}$  transformation the axial length changes recorded by Dantsiger and

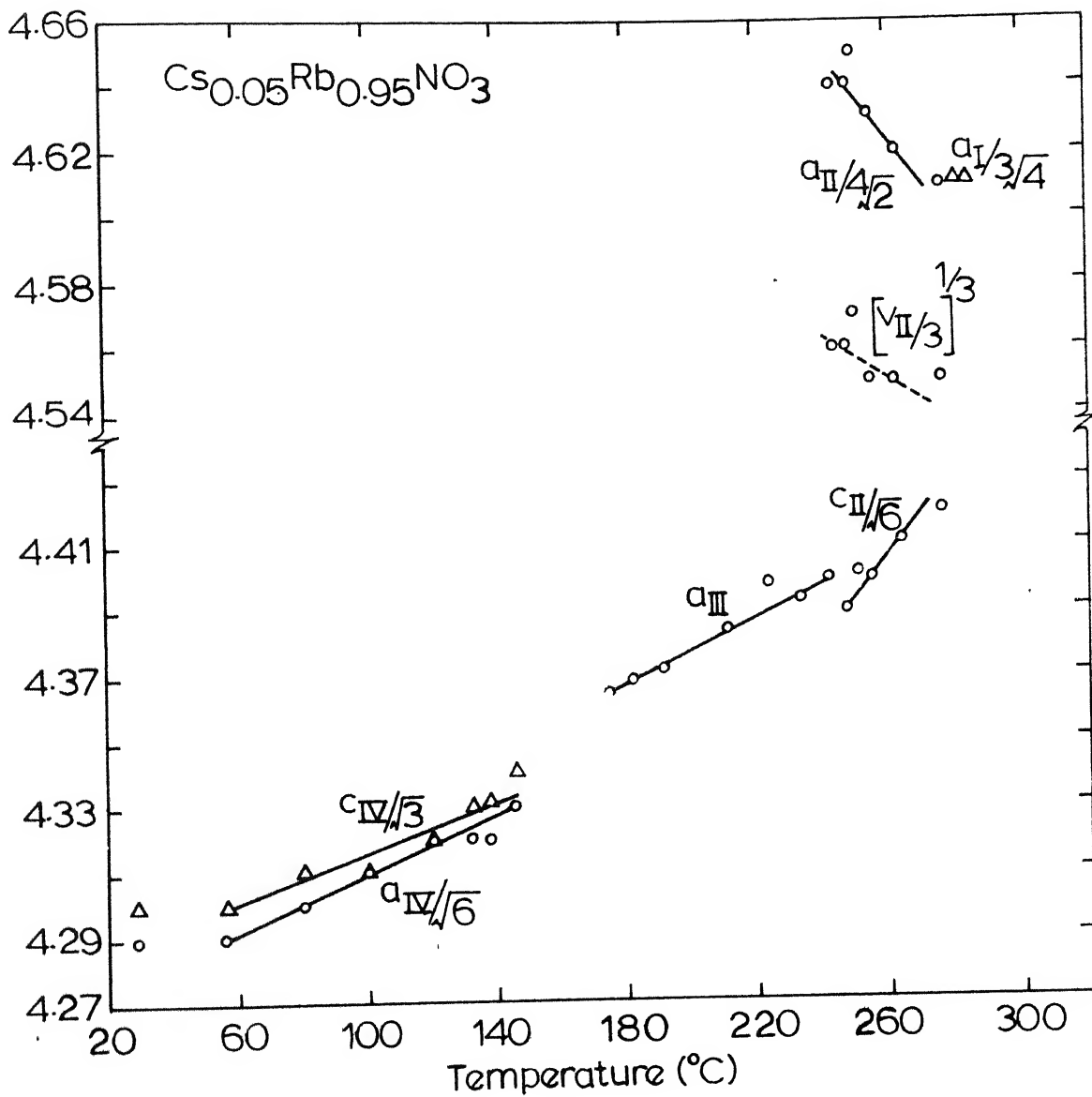


Fig. 4.16: Temperature dependence of reduced lattice parameters of  $\text{Cs}_{0.05}\text{Rb}_{0.95}\text{NO}_3$ . The lattice parameter of each phase are reduced to include one formula weight.

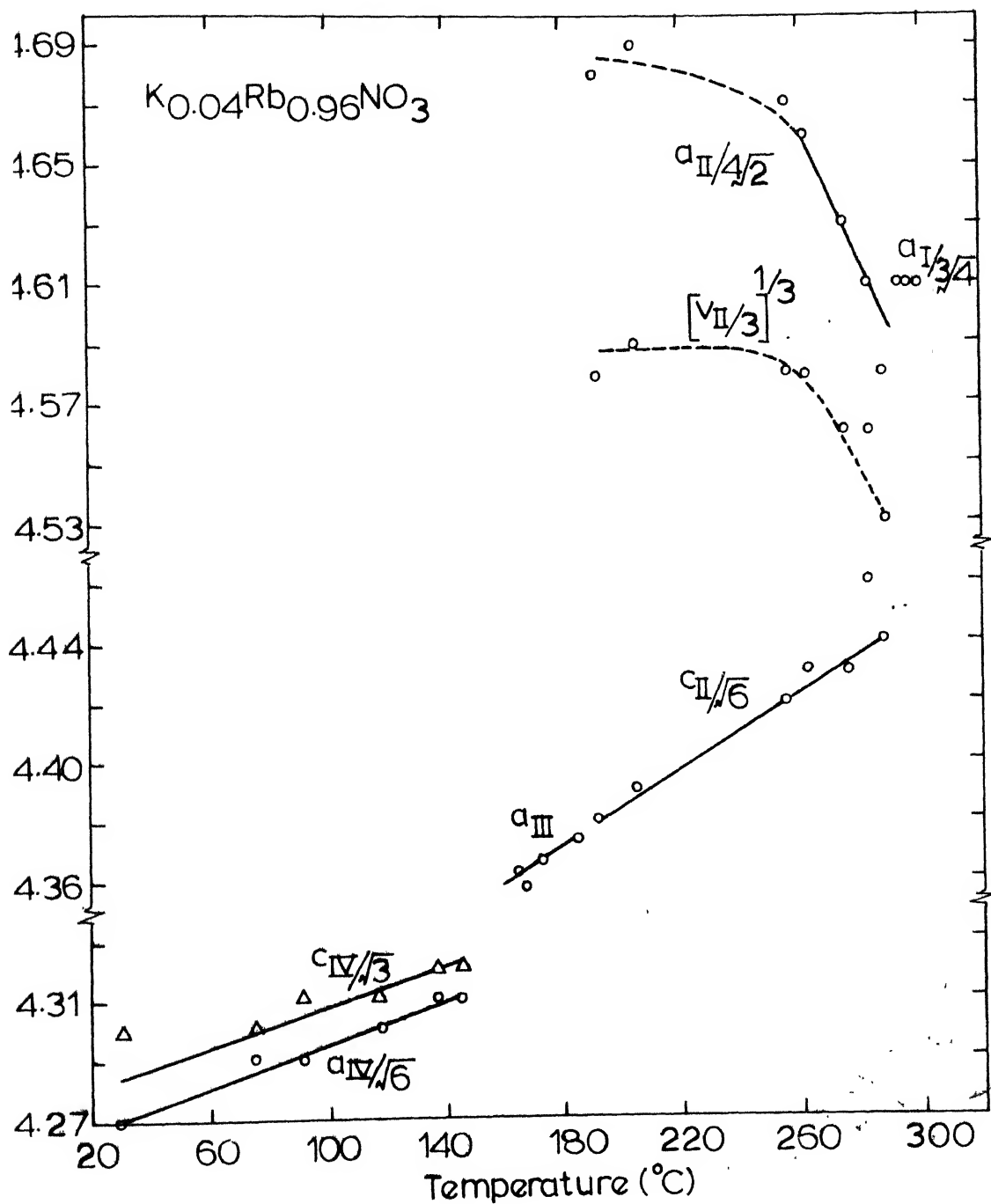


Fig. 4.17 Temperature dependence of reduced lattice parameters of  $\text{K}_{0.04}\text{Rb}_{0.96}\text{NO}_3$ . The lattice parameters of each phase are reduced to include one formula weight.

Fesenko<sup>26</sup>, using a dilatometer, at  $\text{III} \rightarrow \text{II}$  transformation and above cannot be easily compared with the x-ray diffraction study and also the dilatometric study of the polycrystalline material (section 4.3).

The coefficients of linear thermal expansion and percent changes in lattice spacings calculated from the lattice parameter values (figs. 4.15 <sup>to 4.17</sup> ~~15~~) are shown in tables 5.1 and 5.2 respectively.

#### 4.5 Infra-red Absorption

The infrared absorption spectra of  $\text{RbNO}_3$  at different temperatures are shown in figs 4.18 and 4.19. It is seen from these figures that three components are observed in each of the regions of the fundamental modes  $\nu_1$  (1036 to 1056  $\text{cm}^{-1}$ ) and  $\nu_4$  (708 to 764  $\text{cm}^{-1}$ ). Figs 4.18 and 4.20 show that three components are also observed for the mode  $\nu_2$  (816 to 838  $\text{cm}^{-1}$ ) in the room temperature phase. The positions and relative intensities of these modes in different phases of  $\text{RbNO}_3$  are listed in table 4.5.

As the temperature is raised the fundamental absorption peaks in phase IV slightly diminish in intensity as well as show a little shift to the low frequency side (figs 4.18 and 4.19 and Table 4.5).

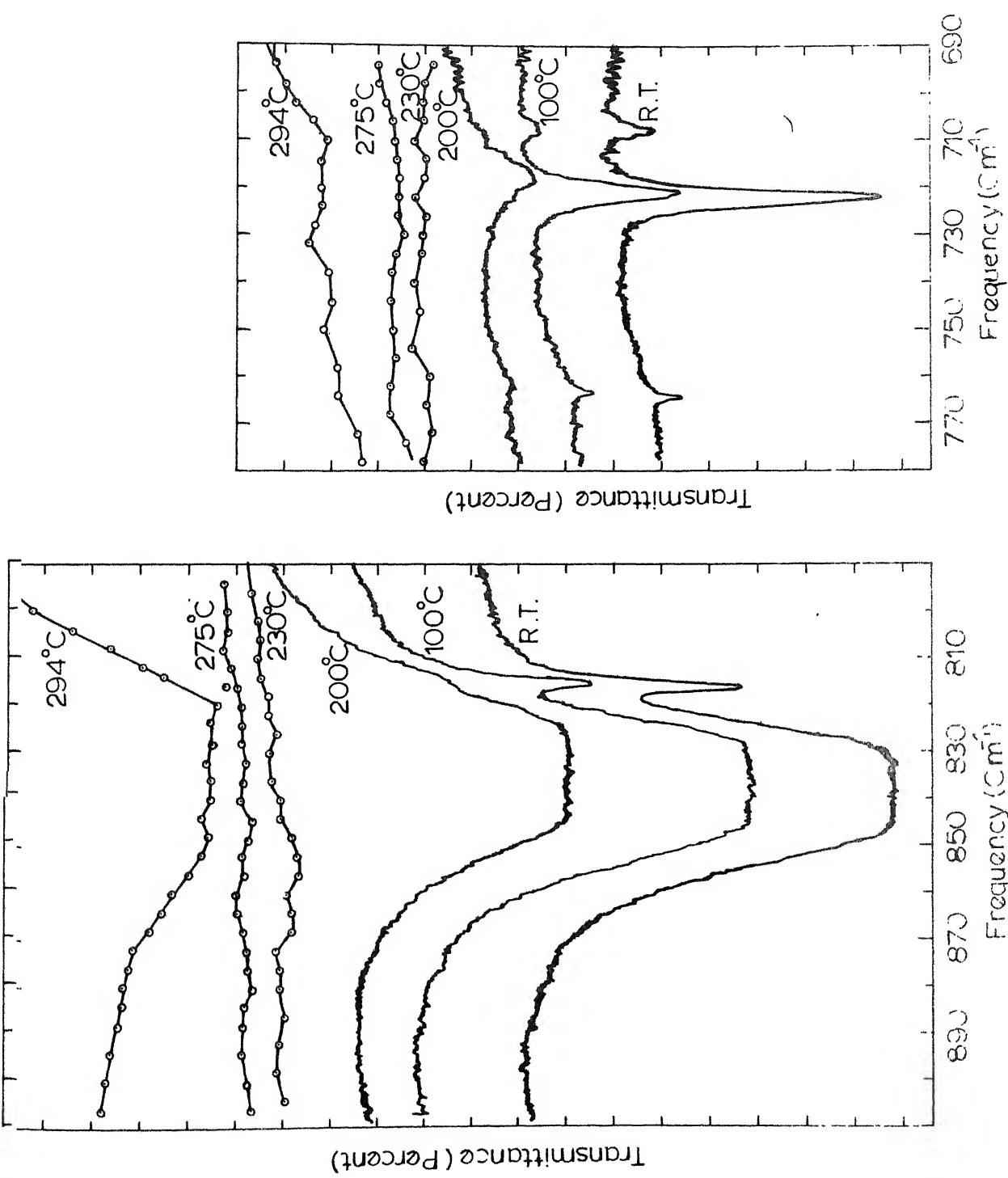


Fig. 4.18: Changes with temperature both in intensity and the number of components of fundamental vibration modes  $\nu_2$  (left) and  $\nu_4$  (right) of  $\text{NO}_3^-$  ion in  $\text{RbNO}_3$ .

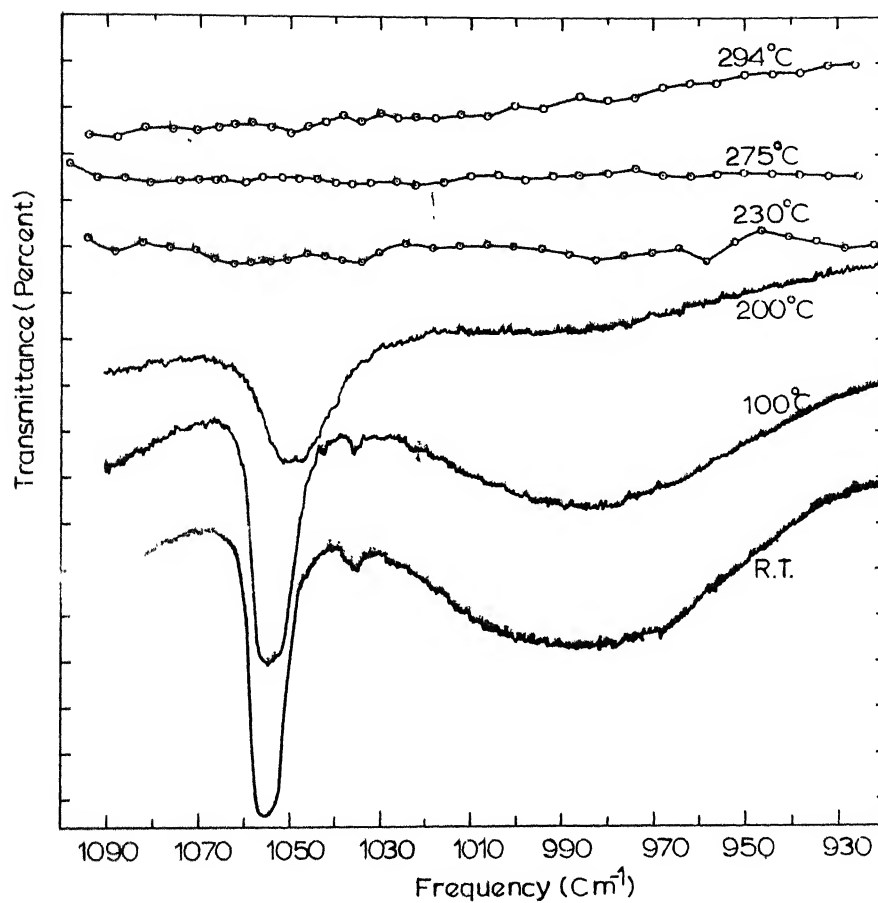


Fig. 4.19 Changes with temperature both in the intensity and the number of components of fundamental vibration mode  $\nu_1$  of  $\text{NO}_3^-$  ion in  $\text{RbNO}_3$ .

TABLE 4.5: Fundamental modes of vibration of  $\text{NO}_3^-$  ion in different phases of  $\text{RbNO}_3$

Phase	Temp. (°C)	$\nu_4$ (cm <sup>-1</sup> )			$\nu_2$ (cm <sup>-1</sup> )			$\nu_1$ (cm <sup>-1</sup> )		
		Component 1	Component 2	Component 3	Component 1	Component 2,3	Component 1	Component 1	Component 2	Component 3
IV	R.T	708W	722ms sharp	764 5V W. sharp	816.5ms sharp	838VS broad	1036V.W. broad	1054S sharp	1056S sharp	
	100	707V.W.	721mV sharp	763.5V.W.	815 5mW.	837V S. broad	1036V.W.	1053.5S sharp	1055S sharp	
III	200	-	718m broad	761.5; V.V.W.	-	834V.S. broad	-	1048ms broad	1051.5ms broad	
	230	-	-	-	-	-	-	-	-	
II	275	-	-	-	-	-	-	-	-	
	294	710? broad	722 broad	-	-	832V S broad	-	1050V.V.W.	-	

Abbreviations: W = weak

V.W. = very weak

V.V.W. = very very weak

m.W. = medium weak

ms = medium strong.

S = strong.

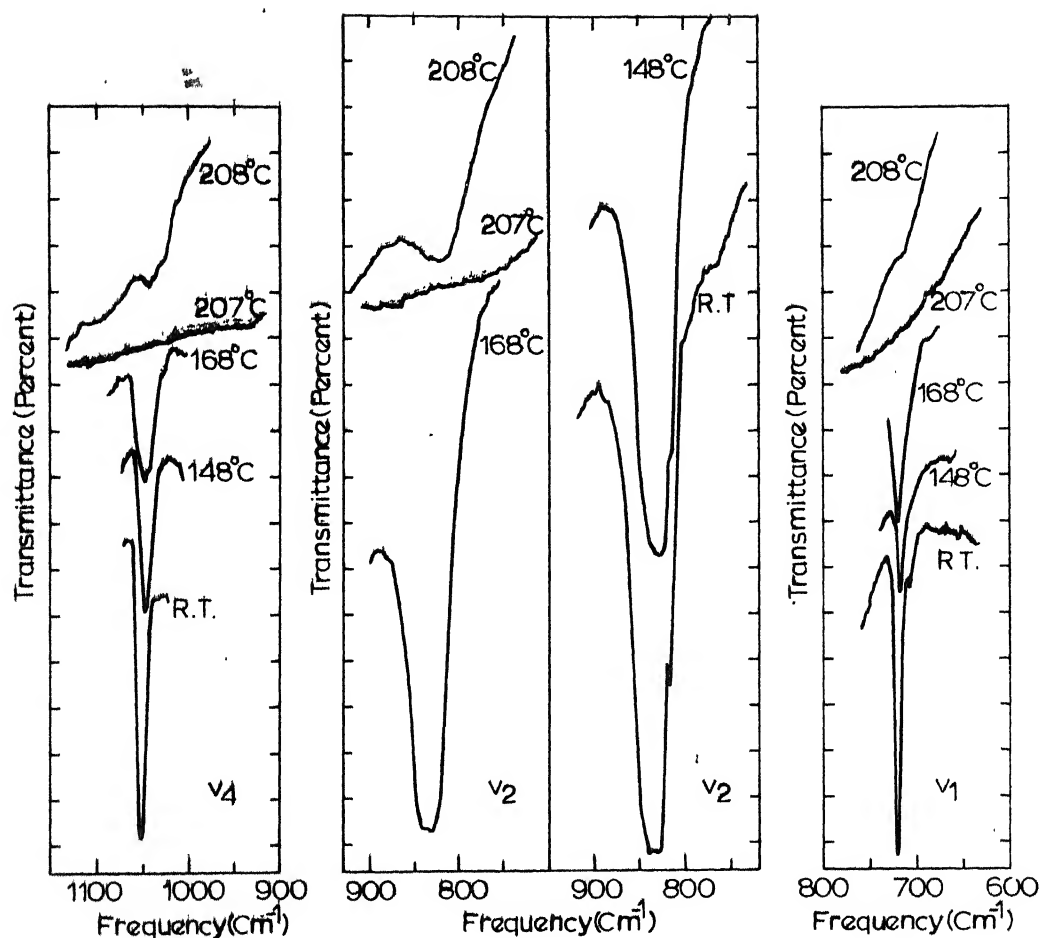


Fig. 4.20 Variation with temperature in the intensity of fundamental modes  $\nu_1$ ,  $\nu_2$  and  $\nu_4$  of  $\text{NO}_3^-$  ion in  $\text{RbNO}_3$ . At 208°C the traces shown were obtained after attenuation of the reference beam.



In phase III each mode has only one component (figs 4.18 and 4.19). As the temperature is raised the fundamental modes  $\nu_1, \nu_2$  and  $\nu_4$  in phase III go on diminishing in intensity. At 207°C their intensity has gone down so much (fig 4.20) that to observe them in this phase the reference beam in the double-beam spectrophotometer has to be attenuated using Perkin-Elmer attenuator attachment. A comparatively large shift in frequency and a slight increase in intensity at IV  $\rightarrow$  III transformation are also observed.

As the temperature is raised above 220°C phase II appears. As already pointed out, the fundamental absorption peaks became too weak to be observed above 207°C. Therefore infrared spectra in phase II at different constant temperatures in the range 230°C upto 280°C were obtained using the techniques described by Greenberg and Hallgren<sup>52</sup> as well as by a suitable attenuation of the reference beam.

At a constant temperature two records of transmittance vs frequency were obtained on the chart paper - one with the shutter of the sample beam open and the other with the shutter of the sample beam closed. The difference of transmittance readings, corresponding to each record, was plotted as a function of frequency. In figs 4.18 and 4.19 the curves at temperatures 230°C, 275°C and 294°C were obtained in this manner.

The above method was adopted by Greenberg and Hallgren<sup>52</sup>

on the following reasoning. When the sample beam shutter is closed the detector is activated by thermal radiation from the infrared cell and the pellet specimen. The specimen may also have specific emission at those wave lengths at which there is maximum absorption. The fact that there are relatively high specific emissions from the specimen is to be expected since  $h\nu$  is of the same order of magnitude as  $kT$ .

It is evident from figs 4.18 and 4.19 that no fundamental absorption peaks ( $\nu_1, \nu_2$  and  $\nu_4$ ) are seen at  $230^\circ\text{C}$  and  $275^\circ\text{C}$  i.e. in phase II.

When temperature is raised to  $285^\circ\text{C}$  phase I appears. Figs 4.18 and 4.19 (at  $294^\circ\text{C}$ ) show that the absorption peaks at fundamental frequencies reappear. The fundamental absorption peaks started appearing to a small extent at  $285^\circ\text{C}$  but became prominent at  $290^\circ\text{C}$  and  $294^\circ\text{C}$  (not shown in figures).

In the solid solutions the spectra at room temperature (figs 4.21 and 4.22) show that  $\nu_1, \nu_2$  and  $\nu_4$  frequencies shift to lower frequencies with  $\text{Cs}^+$  impurity (larger cation size) and to higher frequencies with  $\text{K}^+$  impurity (smaller cation size). Table 4.6 gives a comparative study

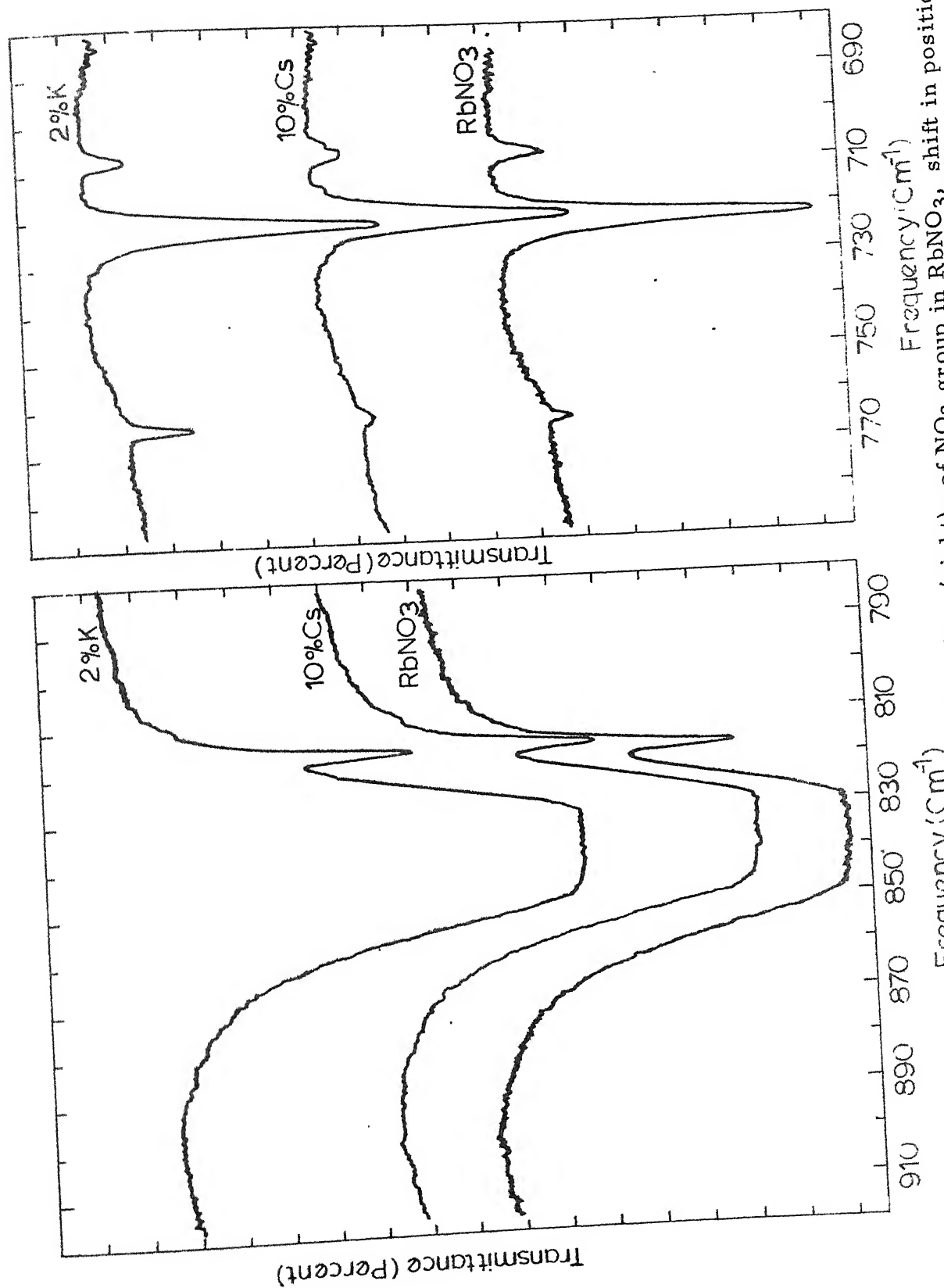


Fig. 4.21: Fundamental modes of vibration  $\nu_2$  (left) and  $\nu_4$  (right), of NO<sub>3</sub> group in RbNO<sub>3</sub>, shift in position as the cation size is changed in the solid solutions Cs<sub>0.10</sub>Rb<sub>0.90</sub>NO<sub>3</sub> and K<sub>0.02</sub>Rb<sub>0.98</sub>NO<sub>3</sub>.  
Traces at room temperature are shown.

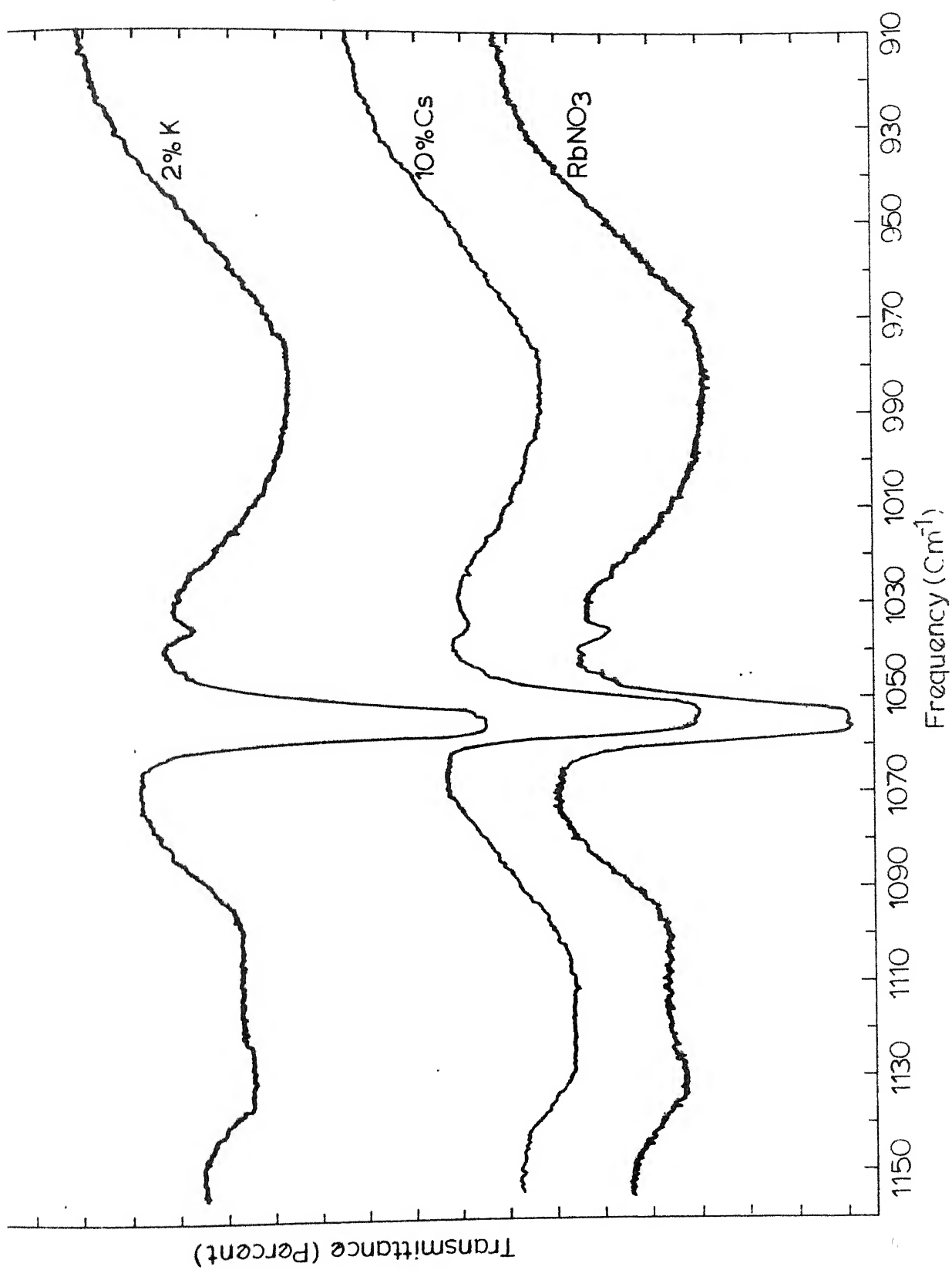


Fig. 4.22: The traces show shift in positions of the fundamental vibration mode  $\nu_1$  at room temperature due to substitution of  $\text{Cs}^+$  or  $\text{K}^+$  ions for the cation in  $\text{RbNO}_3$ .

TABLE 4.6:  $\text{NO}_3^-$  ion fundamental frequencies ( $\nu$   $\text{cm}^{-1}$ ) at room temperature for  $\text{RbNO}_3$  and its solid solutions.

Specimen	$\nu_4$			$\nu_2$		$\nu_1$		
	Component 1	Component 2	Component 3	Component 1	Component 2	Component 1	Component 2	Component 3
$\text{RbNO}_3$	708W sharp	722ms sharp	764.5V.W. sharp	816.5ms sharp	838V S broad	1035.5V.W. broad	1054S sharp	1056S sharp
$\text{Cs}_{0.1}\text{Rb}_{0.9}\text{NO}_3$	707V	721ms	763V.S.	815.5ms sharp	837V S broad	1035V.W. broad	1053S sharp	1055.5S sharp
$\text{K}_{0.02}\text{Rb}_{0.98}\text{NO}_3$	708W	722.5ms	765V sharp	816 5ms sharp	838V S broad	1036V.W. broad	1053S sharp	1056S sharp

Abbreviations are same as in TABLE 4.5.

of fundamental modes of  $\text{NO}_3^-$  ion in the solid solutions at room temperature.

In general the intensities of absorption peaks of fundamentals reduce by  $\text{Cs}^+$  substitution and get enhanced during  $\text{K}^+$  substitution (figs 4.21 and 4.22).

## Chapter 5

### DISCUSSION

#### 5.1 Thermal Properties:

##### 5.1.1 Thermal Expansion Coefficients.

The slopes of the straight line portions of the dilatometric curves, presented in figs. 4.10 and 4.11, represent the coefficients of linear thermal expansion of the stable phases of  $\text{RbNO}_3$  and its solid solutions. These are summarized in table 5.1. Cleaver et al.<sup>2</sup> have given the volume thermal expansion coefficients for phases IV and III of  $\text{RbNO}_3$ . One third values of these coefficients are listed for comparison with those of the present study. Also included in table 5.1 are coefficients of linear thermal expansion of the lattice spacings and  $\frac{1}{3} \frac{\Delta V}{V}$  per  $^{\circ}\text{C}$  from the X-ray data. The coefficients of expansion of lattice constants in phase IV of  $\text{RbNO}_3$  are reported by Kennedy et al.<sup>(17)</sup> (section 1.5). The corresponding values obtained in the present study (Table 5.1) are in reasonable agreement with those.

The  $\alpha_a$  and  $\alpha_c$  values of the hexagonal phase IV are nearly the same and close to the value of linear thermal expansion coefficient obtained from the dilatometric measurement, whereas the  $\alpha$  values of the hexagonal phase II are strongly anisotropic. The  $\alpha$  values determined from the lattice parameters are in fair agreement

TABLE 5.1 Coefficients of linear thermal expansion in different phases of  $\text{RbNO}_3$  and its solid solutions.

Phase	Method of determination.	Coefficient of linear thermal expansion.	$\text{RbNO}_3$		$\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$		$\text{K}_x\text{Rb}_{1-x}\text{NO}_3$	
			Literature values	Present study	x=0.05	x=0.10	x=0.20	x=0.02
	Dilatometry	$\alpha \times 10^6 (^\circ\text{C})^{-1}$	70(2)	102 (92)	97 (83)	93 (83)	99	86
IV	X-ray diffraction	$\alpha_a \times 10^6 (^\circ\text{C})^{-1}$	97.1 (17)	84	104			
		$\alpha_c \times 10^6 (^\circ\text{C})^{-1}$	101.5 (17)	97	86			
		$\frac{1}{3} \frac{\Delta V}{V} \times 10^6 (^\circ\text{C})^{-1}$		101				
III	X-ray diffraction.	$\alpha \times 10^6 (^\circ\text{C})^{-1}$	113(2)	162 (79)	145 (152)	130	122	156
		$\alpha_a \times 10^6 (^\circ\text{C})^{-1}$	85(17)	131	117			
		$\frac{1}{3} \frac{\Delta V}{V} \times 10^6 (^\circ\text{C})^{-1}$		135				



(TABLE 5.1 Contd.)

Phase	Method of determination.	Coefficient of linear thermal expansion.	RbNO <sub>3</sub>			Cs Rb NO <sub>3</sub>		K Rb NO <sub>3</sub>	
			Literature values	Present study		x=0.05	x=0.10	x=0.20	x=0.02
II	Dilatometry	$\alpha \times 10^6 (^{\circ}\text{C})^{-1}$		117 (99)					
	X-ray diffraction	$\alpha_a \times 10^6 (^{\circ}\text{C})^{-1}$		-265	(181')	-288			122
		$\alpha_c \times 10^6 (^{\circ}\text{C})^{-1}$		283		304			142
		$\frac{1}{3} \frac{\Delta V}{V} \times 10^6 (^{\circ}\text{C})^{-1}$		-85					
I	Dilatometry	$\chi \times 10^6 (^{\circ}\text{C})^{-1}$		(55)	(143)				(110)

Dilatometric values given in paranthesis are obtained from cooling curves. The values of  $\chi$  quoted here are  $\frac{1}{3}$  of the coefficient of volume expansion.

with the dilatometric results in phase IV (where the anisotropy of thermal expansion is small) and in phase III (which is cubic) but not in phase II, due to the large anisotropy of axial expansion.

The  $\alpha$  value for phase I recorded in table 5.1 may be smaller than the real value, since the expansion here is likely to be partly offset by the plastic deformation of the sample under the weight of the quartz tube carrying the optical lever. It may be recalled that this phase exists over a narrow temperature range just below the melting point.

#### 5.1.2 Volume and Length Changes at Phase Transitions:

Table 5.2 gives percent changes in length and lattice spacings, at the transition points, from dilatometry (figs. 4.10 and 4.11) and X-ray data (figs 4.14 to 4.17).

The length changes observed here correspond fairly well with the volume changes reported in the literature<sup>(2)</sup> at the various transition points, except for the value reported by Ubbelohde<sup>(2)</sup> at the IV  $\rightarrow$  III transition. Lattice parameter changes were reported by Kennedy et al<sup>(17)</sup> at the IV  $\rightarrow$  III transition and these values agree with the present results in sign but not in magnitude. The difference in the values of the lattice parameter changes observed at the transformation, of the

TABLE 5.2 Percent changes in length at the phase transitions in  $\text{RbIO}_3$  and its

solid solutions.

Transition determi- nation	Method of Length change	$\text{RbIO}_3$		$\text{Cs Rb}_{1-x}\text{NO}_3$		$\text{K Rb}_{1-x}\text{IO}_3$	
		Literature values		Present study		x=0.02	
				x=0.05	x=0.10	x=0.20	x=0.04
IV to III	Dilatometry	$\Delta l/l(\%)$	1.7 <sup>(2)</sup> , 0.7 <sup>(40)</sup> 0.61 <sup>(41)</sup> , 1.7 <sup>(47)</sup>	0.95 (0.55)	0.64 (0.53)	0.81 (0.66)	0.64 (0.44)
	X-ray	$\Delta a/a(\%)$	+0.78 <sup>(17)</sup>	0.23			0.95 (0.62)
	diffraction	$\Delta c/c(\%)$	-0.70 <sup>(17)</sup>	-0.12			0.70
		$\frac{1}{3} \frac{\Delta V}{V}(\%)$		0.05			
III to II	Dilatometry	$\Delta l/l(\%)$	3.33 <sup>(2)</sup> , 4 <sup>(47)</sup>	3.96 (2.75)	3.40 (3.60)	3.56 (4.10)	3.96 (3.96)
	X-ray	$\Delta a/a(\%)$		6.67	5.80		7.10
	diffraction	$\Delta c/c(\%)$		0.07	-0.40		0.14
		$\frac{1}{3} \frac{\Delta V}{V}(\%)$		4.90			

Transition	Method of Length determination	RbNC <sub>3</sub>		Cs <sub>x</sub> Pb <sub>1-x</sub> NO <sub>3</sub>		K <sub>x</sub> Pb <sub>1-x</sub> NO <sub>3</sub>	
		Literature value	Present study	x=0.05	x=0.10	x=0.20	x=0.02
	Dilatometry $\Delta l/l(\%)$	0.33 <sup>(2)</sup> , 1.82 <sup>(47)</sup>	0.44 (0.44)				x=0.02
II to I	X-ray		0.24				
	$\Delta a/a(\%)$		1.18				0.36 (0.46)
	diffraction $\Delta c/c(\%)$		3.50				0.83 3.86
	$\frac{1}{3} \frac{\Delta V}{V}(\%)$		1.70				

The numbers in brackets under the columns-"Present study" and the solid solutions, represent the values obtained from cooling curves whereas superscripts in brackets denote the reference numbers. The dilatometric values are given as  $\Delta V/V(\%)$  in literature. Here only  $\frac{1}{3} (\Delta V/V)$  are tabulated to compare with the values  $\Delta l/l(\%)$  of the present study.  $\Delta a/a$  and  $\Delta c/c$  of the present X-ray study are obtained from the reduced lattice parameter plots i.e. fig. 4.15 to 4.17.

present study and those of Kennedy, may be probably due to the reduced lattice parameters plotted here (fig. 4.15). The relatively small axial changes observed at this transition are indicative of a displacive or order-disorder transformation.

On the other hand, the axial changes at the  $\text{III} \rightarrow \text{II}$  and  $\text{II} \rightarrow \text{I}$  are much larger, suggestive of reconstructive phase changes. The kinking and fragmentation of crystals at the  $\text{III} \rightarrow \text{II}$ , reported by Brown and McLaren<sup>(4)</sup> are no doubt due to the drastic distortion of the crystal lattice. The length changes observed in the present work and the  $\Delta V$  reported by Ubbelohde<sup>(2)</sup> at the  $\text{II} \rightarrow \text{I}$  transition are fairly small, in fact, smaller than at the  $\text{IV} \rightarrow \text{III}$  transformation. However, the X-ray data shows substantial changes at the  $\text{II} \rightarrow \text{I}$  transition, though not as large as at the  $\text{III} \rightarrow \text{II}$  phase change. The reason for not recording large length changes with the dilatometer as the X-ray data suggest may be because the sample may have become plastically deformed.

### 5.1.3 Difference in the Thermal Expansion Plots of Dilatometric and X-ray Studies:

Fig. 5.1 shows a plot (continuous curve) of  $\Delta l/l$  vs temperature from the dilatometric data on heating and (broken curve)  $\frac{1}{3} \left( \frac{\Delta V}{V} \right)$  vs temperature from the X-ray data, obtained

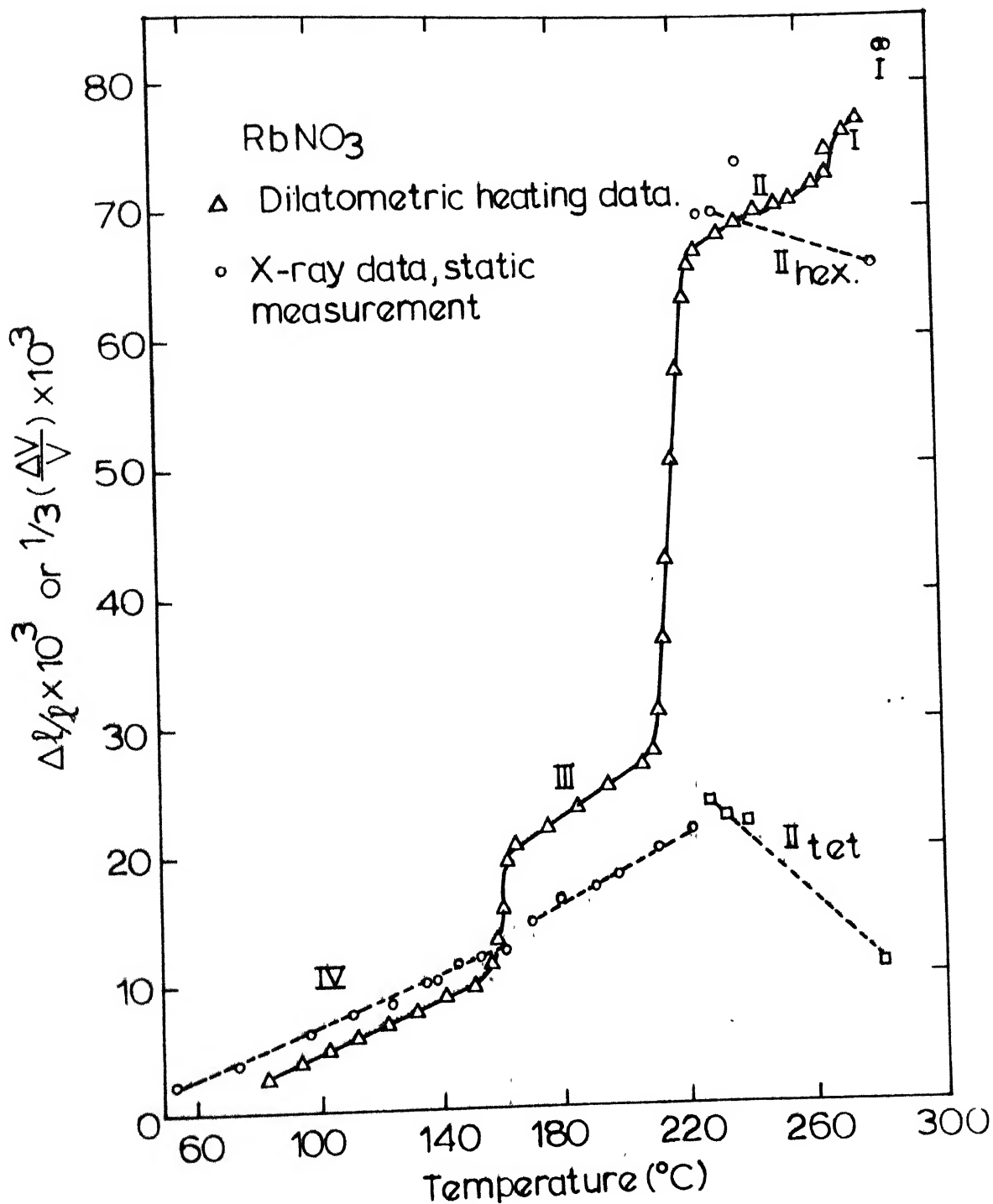


Fig. 5.1 Thermal expansion data from dilatometry ( $\Delta l/l$ ) during heating and X-ray data ( $1/3(\Delta V/V)$ ), obtained after thermal equilibrium has been attained. I, II, III and IV denote solid phases of  $\text{RbNO}_3$ . X-ray data for the tetragonal ( $\text{II}_{\text{tet}}$ ) and hexagonal ( $\text{II}_{\text{hex}}$ ) structures of phase II are shown.

at indicated temperatures after equilibration. The symbols I, II, III and IV represent the different solid phases of  $\text{RbNO}_3$  (section 1.2). It is clear from the figure that at  $\text{IV} \rightarrow \text{III}$ ,  $\text{III} \rightarrow \text{II}$  and  $\text{II} \rightarrow \text{I}$  transformations both data show thermal expansion while in phase II contraction is observed by X-ray measurements and expansion by dilatometric studies.

It may be seen from fig. 4.14 that, (i) after  $\text{III} \rightarrow \text{II}$  transformation there is expansion along the c-axis in phase II and (ii) contraction along the a-axis of phase II. The result is that  $\frac{1}{3} \left( \frac{\Delta V}{V} \right)$  vs temperature plot declines at higher temperatures (fig. 5.1). To explain the expansion in phase II (as seen in the dilatometric curve) it seems reasonable to conclude that, after  $\text{III} \rightarrow \text{II}$  transformation, there is some preferred orientation along the c-axis which shows expansion, as observed by X-ray data. Therefore, the dilatometer, which measures expansion only in one direction (i.e. along the length of the rod specimen), records expansion (see also Table 5.1)

For phase II, both the tetragonal and hexagonal cell parameters are used in plotting  $\frac{\Delta V}{V}$  vs temperature in fig 5.1. It is clear that the large thermal expansion at the  $\text{III} \rightarrow \text{II}$  transformation and the smaller one at the  $\text{II} \rightarrow \text{I}$  transition,

observed in the dilatometric experiment, cannot be accounted for on the basis of a tetragonal cell for phase II. The hexagonal cell on the other hand, gives a satisfactory agreement between the dilatometric and X-ray results.

#### 5.1.4 Co-existence of Phases and Thermal Hysteresis in the Transformation Regions:

According to Ubbelohde<sup>(69)</sup> the phenomena of thermal hysteresis can be readily understood on the basis of coexistence of phases in the transformation regions. For instance, if phase 1 transforms to 2 by a volume expansion, then 2 is growing in a matrix of 1 and is under compression. In the reverse transformation 1 is in the matrix of 2 and is under tension. So the two paths for the transformation are not identical, which gives rise to hysteresis.

The transformation regions for  $IV \rightleftharpoons III$  and  $II \rightleftharpoons I$  are quite narrow. Very good temperature control is essential to see the coexistence of phases in these regions. Kennedy, Taylor and Patterson<sup>(21)</sup> have used micro-thermostat and polarised light to see the coexistence of phases in  $IV \rightleftharpoons III$  transformation region and have reported a temperature hysteresis of  $0.1^{\circ}\text{C}$  in fresh crystals. The maximum hysteresis was found to be  $1^{\circ}\text{C}$ .



after recycling this transformation several times.

In  $\text{III} \rightleftharpoons \text{II}$  transformation coexistence of phases in the transformation region is readily established by X-ray diffraction methods. The (110) reflection is characteristic of phase III and (102) is characteristic of phase II. In the transformation range, the temperature was held constant at different values and (110) and (102) reflections recorded by slow scanning. Fig. 5.2 shows the data for  $\text{K}_{0.04}^{\text{Rb}}\text{NO}_3$ . At  $195^\circ\text{C}$ , only phase III is present. On heating to  $208^\circ$  and  $222^\circ\text{C}$ , the intensity of the (110) line of phase III gradually decreases as that of the (102) line of phase II increases and finally, at  $225^\circ\text{C}$ , phase III disappears completely. On cooling, phase III does not appear until the sample is cooled to  $206^\circ\text{C}$ , which is  $19^\circ\text{C}$  below the temperature at which it disappeared on heating. The amount of phase III increases at the expense of phase II on further cooling to  $203^\circ$ ,  $198^\circ$ , and  $192^\circ\text{C}$  and only at  $185^\circ\text{C}$  does phase II disappear almost completely. Thus the coexistence of phases in the transformation region and the temperature hysteresis are clearly seen in fig. 5.2. This coexistence of phases along with the thermal hysteresis can also be seen by referring to fig. 5.5.

Thermal hysteresis at the phase transformations is easily seen by referring to the conductivity plots (fig.4.1 & 4.2)

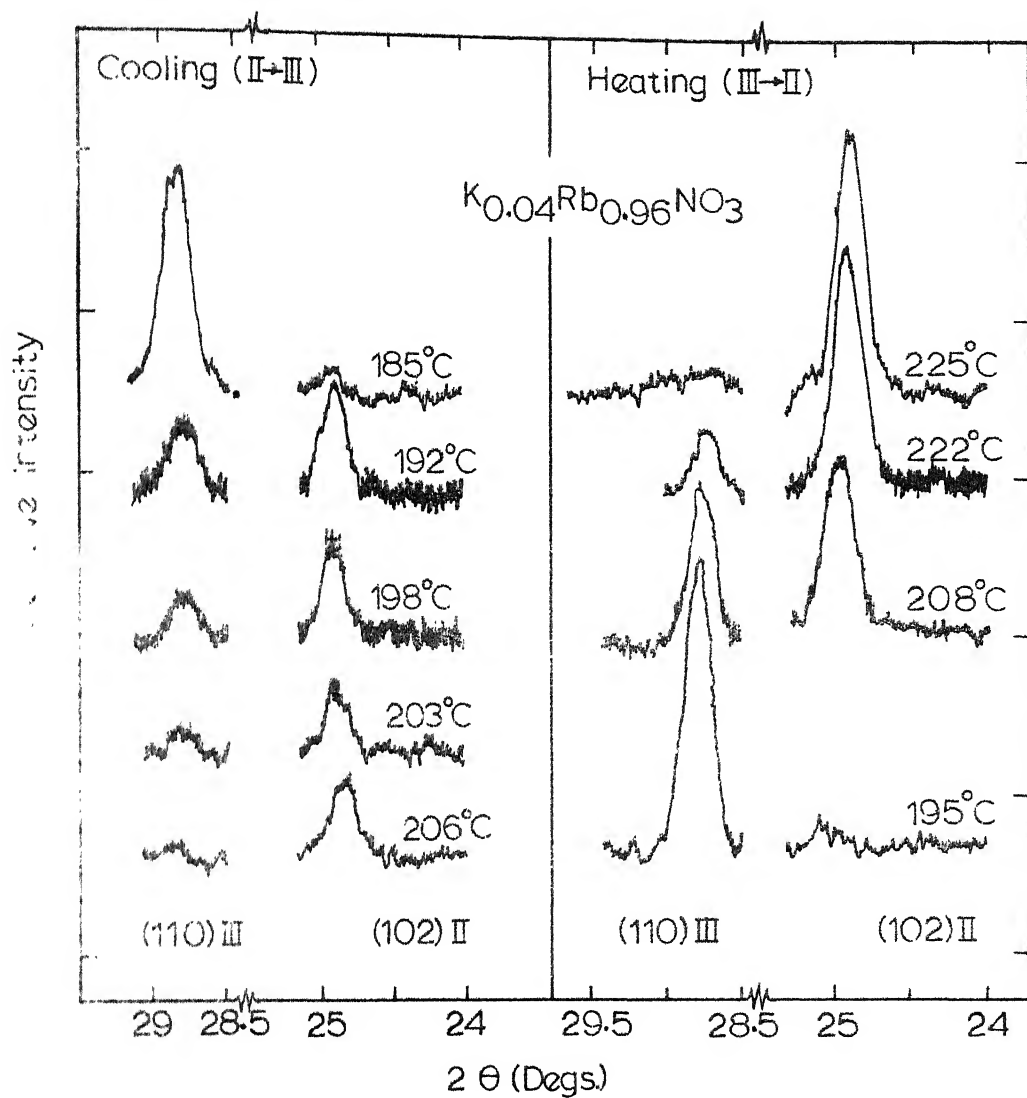


Fig. 5.2 Thermal hysteresis and co-existence of phases III and II in  $\text{K}_{0.04}\text{Rb}_{0.96}\text{NO}_3$ .

and dilatometric curves (figs 4.10 & 4.11). Thermal hysteresis curves shown in fig. 5.3 for  $IV \rightleftharpoons III$  and  $III \rightleftharpoons II$  transformations are drawn from the differential thermograms<sup>(Appendix E)</sup>. These curves plot the amount transformed vs temperature, obtained from heating and cooling curves. The amount transformed is the ratio of the height of a point on the DTA curve (peak) to its maximum height. This method of plotting the hysteresis loops from DTA curves follows that of Rao and Rao<sup>(47)</sup>.

Temperature hysteresis in  $III \rightleftharpoons II$  transformation has also been studied by static and dynamic methods using X-ray diffraction. In the dynamic method, plotting the height of the characteristic X-ray diffraction line (which is proportional to the fraction of the transformed phase) as a function of temperature during heating and cooling gives the hysteresis loops for the materials under study. The hysteresis loops so obtained are shown in fig. 5.4. The slope of the vertical portion of the hysteresis loop, in case of  $RbNO_3$ , shows that the transformation is quite sudden whereas it grows sluggish with increasing concentration of  $Cs^+$  or  $K^+$ , the hysteresis loops become increasingly slanted with concentration. The hysteresis in temperature decreases with  $Cs^+$  concentration as compared with the pure material. Reverse is the case with  $K^+$

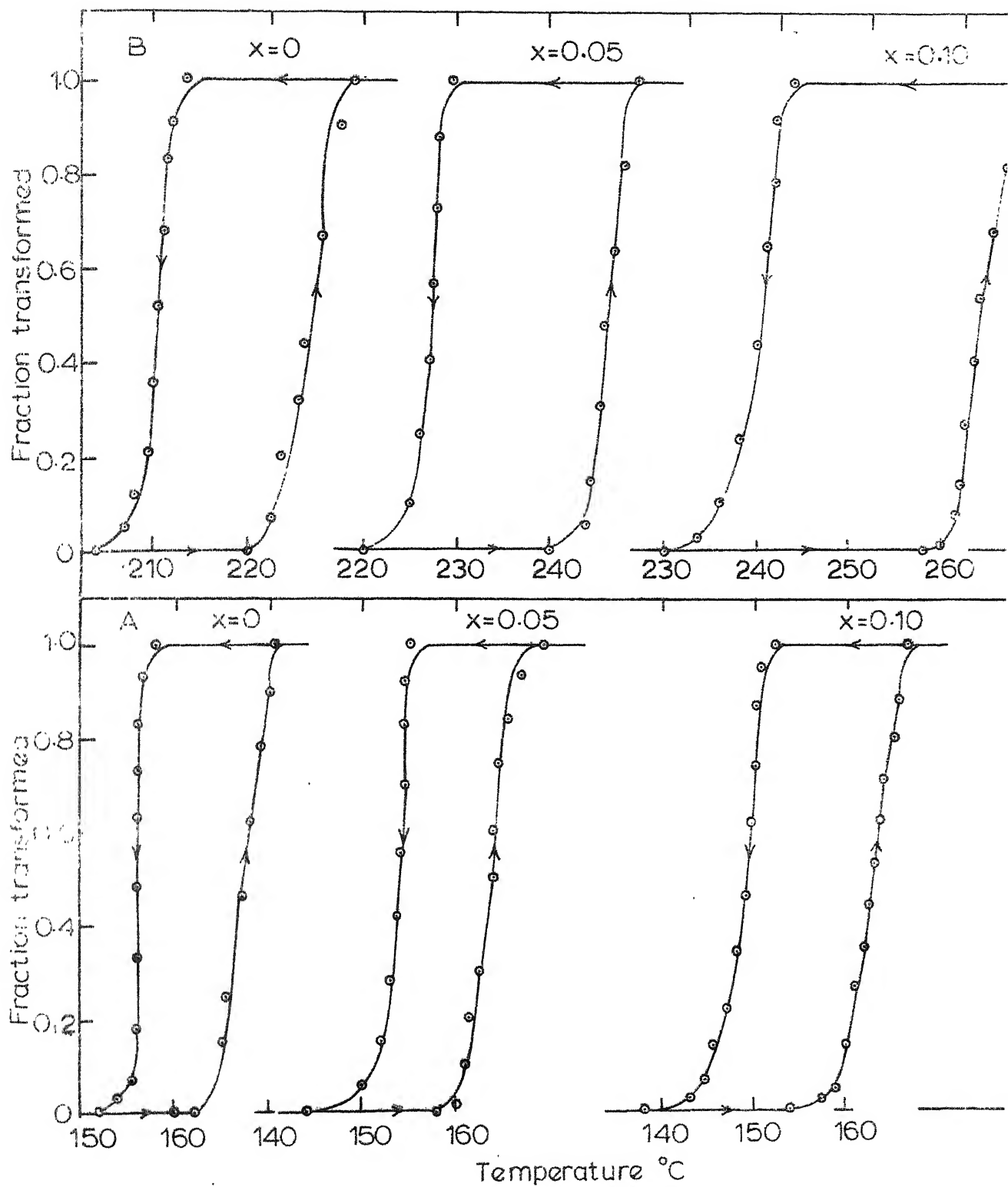


Fig. 5.3 Thermal hysteresis loops in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system from DTA curves (A) IV  $\rightleftharpoons$  III transformation, (B) III  $\rightleftharpoons$  II transformation.

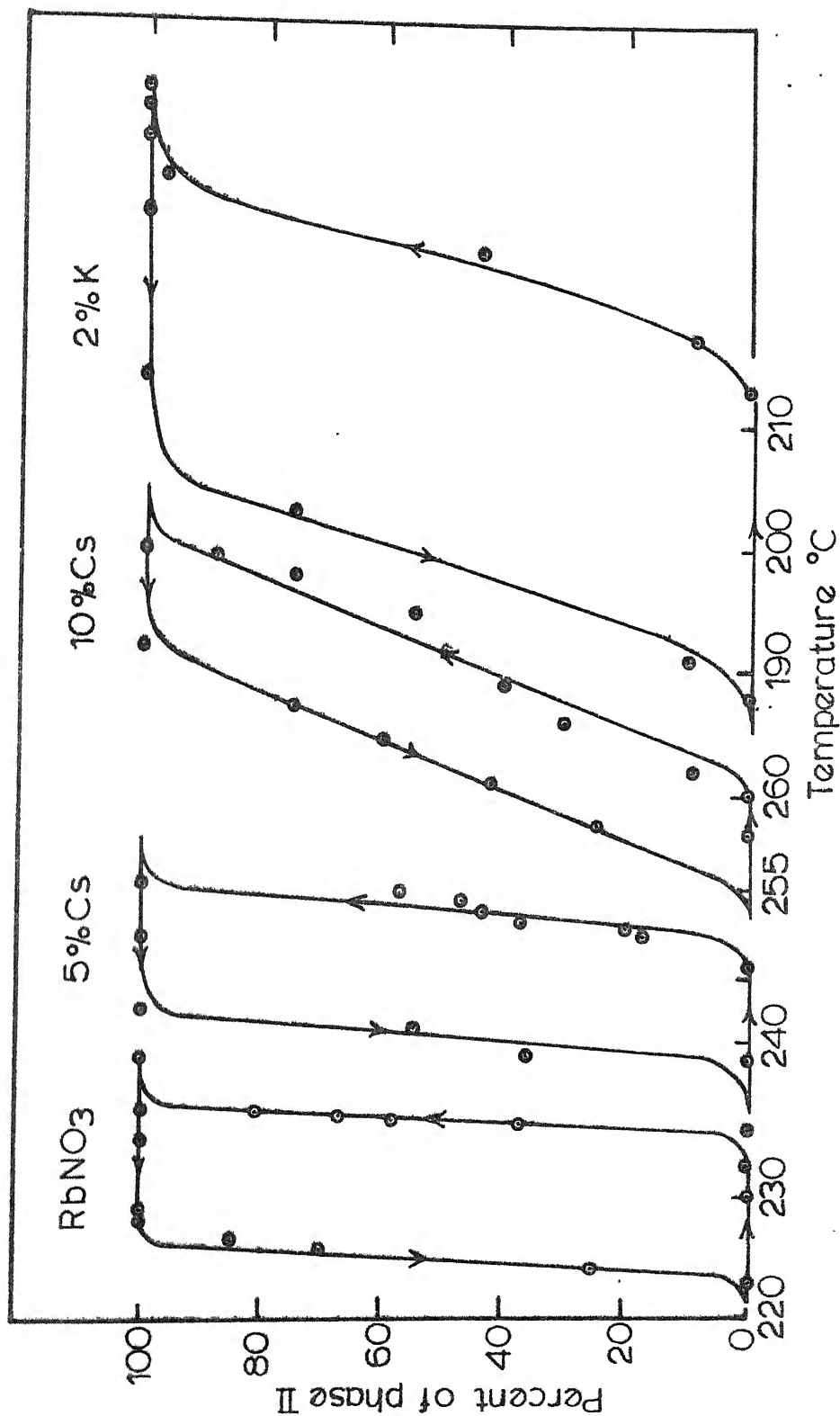


Fig. 5.4: X-ray determination of thermal hysteresis by dynamic method at III-II transformation in RbNO<sub>3</sub>, Cs<sub>0.05</sub>Rb<sub>0.95</sub>NO<sub>3</sub>, Cs<sub>0.10</sub>Rb<sub>0.90</sub>NO<sub>3</sub>, Cs<sub>0.20</sub>K<sub>0.80</sub>Rb<sub>0.98</sub>NO<sub>3</sub>.

concentration. In this connection a remark may be made about the wide vertical hysteresis loop obtained for  $\text{Cs}_{0.10}\text{Rb}_{0.90}\text{NO}_3$  at  $\text{III} \rightleftharpoons \text{II}$  transformation from DTA curves (fig 5.3). The heating and cooling differential thermograms are not traced separately for  $\text{III} \rightleftharpoons \text{II}$  transformation due to its closeness to  $\text{II} \rightleftharpoons \text{I}$  transformation and due to high rate of heating (as compared with other methods of study) and uncontrolled cooling the spread of peaks is not properly shown by DTA curves and hence instead of getting a slanted loop (as determined by X-ray studies (fig 5.4)) a wide vertical loop is obtained.

In the static method, the height of the (102) peak, which gives the amount of phase II transformed, is plotted versus temperature. This yields a hysteresis loop. Plotting the peak heights for (110) reflection during heating and cooling gives the amount of phase III transformed vs temperature. Overlap of loops shows coexistence of phases in the transformation region (see fig 5.5). This figure is representative of the data on the co-existence of phases in  $\text{III} \rightleftharpoons \text{II}$  transition region. This is shown here for  $\text{K}_{0.04}\text{Rb}_{0.96}\text{NO}_3$  for the reason that the co-existence of phases is observed over a larger temperature range than in the case of the pure material and other solid solutions. The width

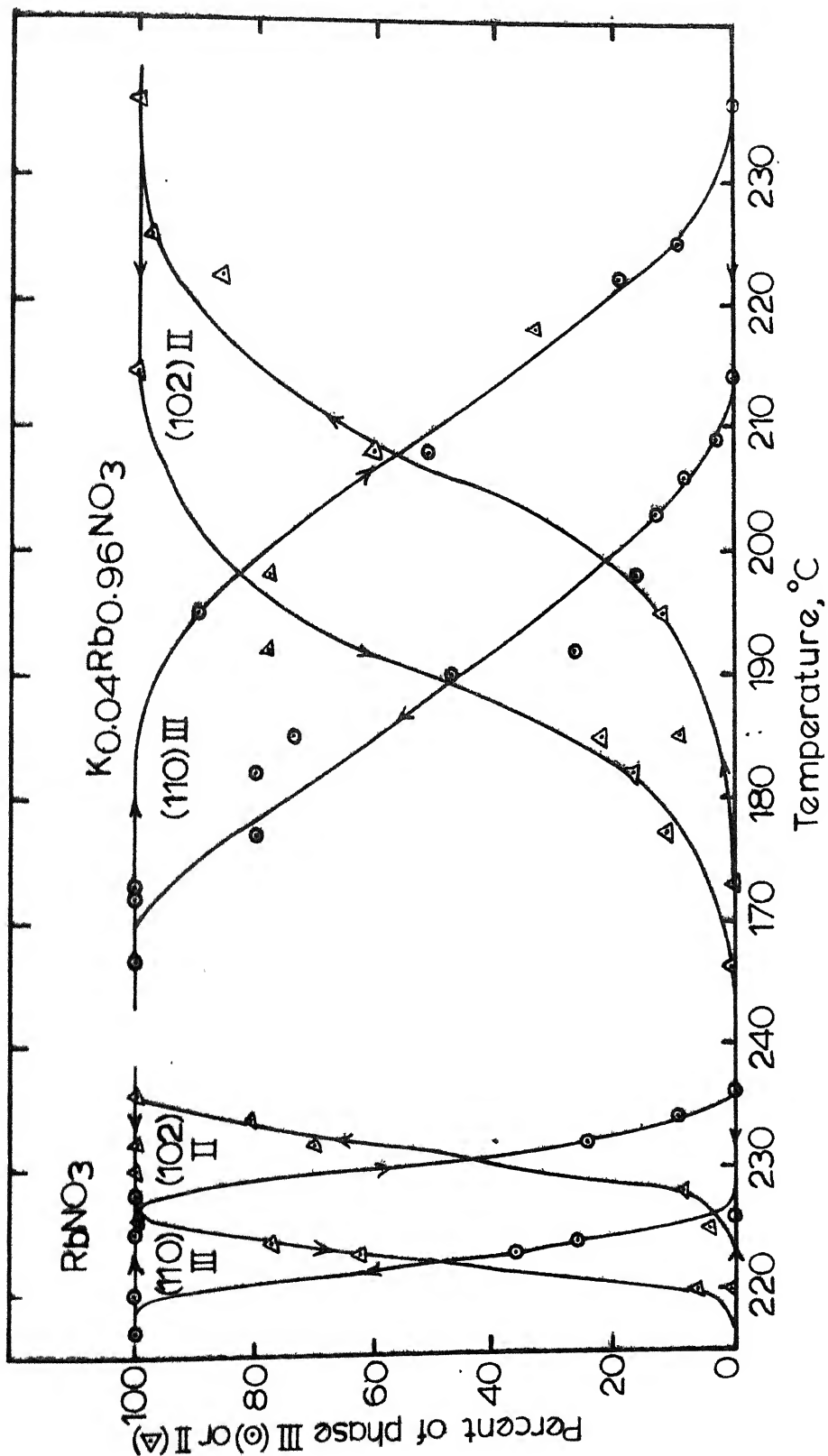


Fig. 5.5: Thermal hysteresis and coexistence of phases III and II in transition region III $\rightleftharpoons$ II(static method).

of the loops in the present case is smaller than in the dynamic method. This is probably due to the fact that thermal hysteresis is a function of rate of temperature change.

The extensive solubility of  $\text{CsNO}_3$  in  $\text{RbNO}_3$  compared to rather small solubility of  $\text{KNO}_3$  in  $\text{RbNO}_3$  suggests that  $\text{Cs}^+$  ions can be accommodated in the  $\text{RbNO}_3$  lattice much more easily than  $\text{K}^+$  ions without large strain or distortion. The large strain associated with the introduction of  $\text{K}^+$  ions in  $\text{RbNO}_3$  lattice gives rise to wide thermal hysteresis loops compared to those obtained with  $(\text{Cs}, \text{Rb})\text{NO}_3$  solid solutions.

Table 5.3 lists the change in volume (calculated from X-ray data) on transformation vs width of the hysteresis loop for  $\text{RbNO}_3$ ,  $\text{Cs}_{0.05}\text{Rb}_{0.95}\text{NO}_3$  and  $\text{K}_{0.04}\text{Rb}_{0.96}\text{NO}_3$ . This table indicates increasing hysteresis width with increasing change in volume at a transformation e.g.  $\text{III} \rightleftharpoons \text{II}$  transformation, for a given composition, exhibits largest hysteresis and largest volume change. Rao and Rao<sup>(47)</sup>, who plotted the change in molar volume at the transformation temperatures vs area of the thermal hysteresis loops for various materials including  $\text{RbNO}_3$  also find a similar relationship.



TABLE 5.3: Change in volume at the transformations ( $\Delta V$ ) and width of the hysteresis loops ( $\Delta T$ ) for  $\text{RbNO}_3$ ,

$\text{Cs}_{0.05}\text{Rb}_{0.95}\text{NO}_3$  and  $\text{K}_{0.04}\text{Rb}_{0.96}\text{NO}_3$ .

Phase transition	$\text{RbNO}_3$		$\text{Cs}_{0.05}\text{Rb}_{0.95}\text{NO}_3$		$\text{K}_{0.04}\text{Rb}_{0.96}\text{NO}_3$	
	$\Delta V(\text{\AA}^3)$	$\Delta T(^{\circ}\text{C})$	$\Delta V(\text{\AA}^3)$	$\Delta T(^{\circ}\text{C})$	$\Delta V(\text{\AA}^3)$	$\Delta T(^{\circ}\text{C})$
IV $\rightleftharpoons$ III	0.84	9	1.00	10	1.70	5
III $\rightleftharpoons$ II	11.38	18	9.64	20	12.85	36
II $\rightleftharpoons$ I	4.73	6	3.46	13	5.10	4

$\Delta V$  values are calculated from the X-ray data and  $\Delta T$  from dilatometric data.

## 5.2 Crystallography of $\text{RbNO}_3$ :

As already seen,  $\text{RbNO}_3$  has four crystalline phases.

The room temperature phase, called phase IV, is known to have a trigonal symmetry with  $a = 10.49\text{\AA}$ ,  $c = 7.44\text{\AA}$  and  $Z = 9$  at room temperature. The space group is  $P3_112$  or  $P3_212^{(4)}$ . Finbak et al<sup>(13)</sup> have given only the  $\text{Rb}^+$  positions in the lattice (fig. 5.7), the  $\text{NO}_3^-$  positions are indicated by Pauling and Sherman<sup>(68)</sup> in fig. 5.14. The lattice parameters determined by various authors have been compared in table 4.4. The lattice parameters at room

temperature, determined in the present study, agree very well with those reported in literature.

Phase III is cubic with Cesium Chloride type structure and  $a = 4.36\text{\AA}$ ,  $Z = 1$  at  $190^{\circ}\text{C}$ . The space group is  $\text{Pa}\bar{3}^{(11)}$ . Korhonen<sup>(11)</sup>, who gave a detailed structural analysis for this phase found that  $\text{NO}_3$  groups are situated on the body diagonals slightly away from the centre, hence he proposed a cell of double this size (fig 5.15). The results, about the space group and lattice constant of this phase, are summarized in section 1.2 and table 4.4

Phase I is known to be cubic with Sodium Chloride type structure. The cube edge is found to be  $7.32\text{\AA}$ , a value close to the one reported by Brown and McLaren<sup>(4)</sup>.

Phase II was investigated in 1937 by Finbak et al<sup>(13)</sup>, for the first time, by powder X-ray diffraction techniques at  $250^{\circ}\text{C}$ . It was reported to have a hexagonal symmetry. The cell parameters found were  $a = 5.48\text{\AA}$  and  $c = 10.71\text{\AA}$  with  $Z = 3$ . The corresponding rhombohedral parameters were  $a = 4.77\text{\AA}$ ,  $\alpha = 70^{\circ} 10'$  and  $Z = 1$ . In 1962, Brown and McLaren<sup>(4)</sup> reinvestigated this phase and proposed a number of possible unit cells for this phase. Based on the closeness of fit and an apparently simple relationship between the

cell parameters of phases II and III, Brown and McLaren proposed a tetragonal cell for this phase with lattice constants  $a = 6.19\text{\AA}$ ,  $c = 8.74\text{\AA}$  and  $Z = 4$ .

An indexed X-ray diffraction pattern for phase II is shown in table 5.4. This table shows that both the tetragonal ( $a = 6.16\text{\AA}$  and  $c = 8.73\text{\AA}$ ) and the hexagonal ( $a = 5.51\text{\AA}$ ,  $c = 10.74\text{\AA}$ ) cells fit equally well for this phase. So the only reason, for Brown and McLaren to prefer a tetragonal cell for this phase, seems to be the simple relationship between phases III and II. It was also reported<sup>(4)</sup> that  $\text{RbNO}_3$  crystals crack and bend at III  $\rightarrow$  II transformation. In view of this disruptive nature of the transformation, a simple relationship between phases III and II, does not seem to be an essential requirement.

In fig. 5.1 is plotted  $\frac{1}{3} \frac{\Delta V}{V}$  vs temperature, from the X-ray data, to compare with the corresponding dilatometric data. For phase II, this plot is shown both for the tetragonal and the hexagonal cells. It is evident that the hexagonal symmetry for phase II is definitely the better choice.

Further support for the above choice can be derived from the density calculations based on the dilatometric and the X-ray data. This is shown in table 5.5. The calculated density values

TABLE 5.4 Observed and calculated 'd' values for the hexagonal and tetragonal structures of phase II of  $\text{PbTiO}_3$

Observed 'd' ( $\text{\AA}^\circ$ )			Hexagonal cell		Tetragonal cell	
FHS <sup>13</sup>	BM <sup>4</sup>	Present study	d cal	h kl	d cal	h kl
4.25	4.36	4.35	4.36	101	4.36	002
3.53	3.57	3.58	3.58	003	3.56	102
2.72	2.77	2.76	2.76	110	2.75	210
2.31	2.34	2.34	2.34	104	2.33	212
2.18	2.19	2.19	2.18/2.18	202/113	2.18	004
	1.96		1.96	105	1.95	222
1.77	1.79		1.79	006	1.78	312
1.70	1.72		1.71	212	1.71	320
	1.60		1.59	300	1.59	322
1.50	1.50		1.50/1.50	116/214	1.49	410
1.45	1.46		1.46/1.45	107/303	1.45	330

TABLE 5.5 (Structural parameters and) density, calculated from the X-ray and dilatometric data, at different temperatures.

Phase	Temperature (°C)	Lattice Parameters (Å)	Z	Density calculated from X-ray data (g/c c)	Density calculated from dilatometric data (g/c c)	Observed density (70)	Crystal structure
IV	29	$a_R = 6.54$		3.11	3.11	3.11	Rhombohedral
	161	6.63	3	3.00	2.99	2.99	
	29	$a_H = 10.45$		3.11	3.11	3.11	Hexagonal
	161	10.63	5	3.00	2.99	2.99	
III	170	$a = 4.347$	1	2.98	2.93	2.93	Cubic
	222	4.376		2.92	2.85	2.87	

(TABLE 5.5 contd. )

Phase	Temperature (°C)	Lattice Parameters (Å°)	* Z	Density calculated from X-ray data (g/c.c)	Density calculated from dilato- metric data (g/c.c)	Observed density (7C.)	Crystal structure
	227	$a_R = 4.80$	$\alpha_R = 70^\circ 43'$	1	2.56	2.57	Rhombohedral
	281	4.81	$69^\circ 8'$		2.62	2.52	
II	227	$a_H = 5.55$	$c_H = 10.69$	3	2.56	2.57	Hexagonal
	281	5.47	10.80		2.60	2.52	
	227	$a_T = 6.21$	$c_T = 8.75$	4	2.91	2.57	Tetragonal
	281	6.11	8.71		3.01	2.52	
I	289	$a = 7.32$	4	2.50	2.49		Cubic

\*  $a_R$  and  $\alpha_R$  are the lattice constants of the Rhombohedral cell  $a_H$  and  $c_H$  represent the parameters for the Hexagonal cell and  $a_T$ ,  $c_T$  for the Tetragonal cell.

in phase II compare reasonably well with those based on the hexagonal symmetry for this phase. The calculated density values, based on the tetragonal cell do not agree at all with those determined from dilatometric data. The density values for the other phases calculated from the dilatometric and X-ray data are in good agreement. Also the observed values of density<sup>(70)</sup> in phases IV and III of  $\text{RbNO}_3$  are very close to those calculated from the dilatometric data and also from the X-ray data.

Based on the number of formula units a probable hexagonal cell with cation positions is proposed in fig. 5.6. The true symmetry for phase II can only be established unambiguously by single crystal X-ray study. However, attempts to retain the crystal in a sound condition on heating to  $250^\circ\text{C}$ , in the present study as well as by earlier workers, have been unsuccessful.

#### 5.2.1 Lattice Relationships between the four Phases of $\text{RbNO}_3$ .

#### 5.2.2 IV and II relation:

Finbak et al<sup>(13)</sup> have shown a relation between the hexagonal phase IV and the cubic phase III in fig. 5.7. It is easy to write down with the help of this diagram that

$$3a_{\text{III}} = \sqrt{a_{\text{IV}}^2 + c_{\text{IV}}^2} \quad (1)$$

(2)

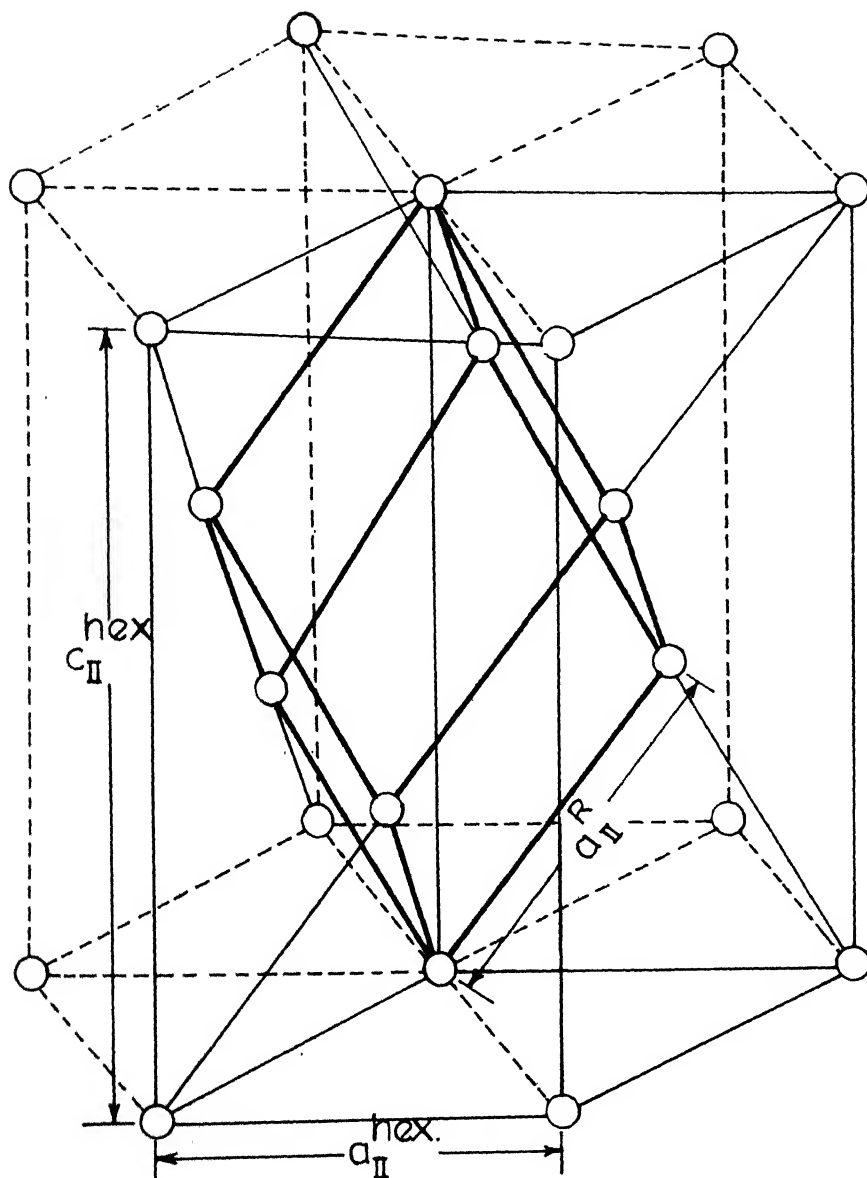


Fig. 5.6: Proposed hexagonal cell of phase II. The corresponding rhombohedral cell is also shown by thick lines. Circles indicate the cation positions.



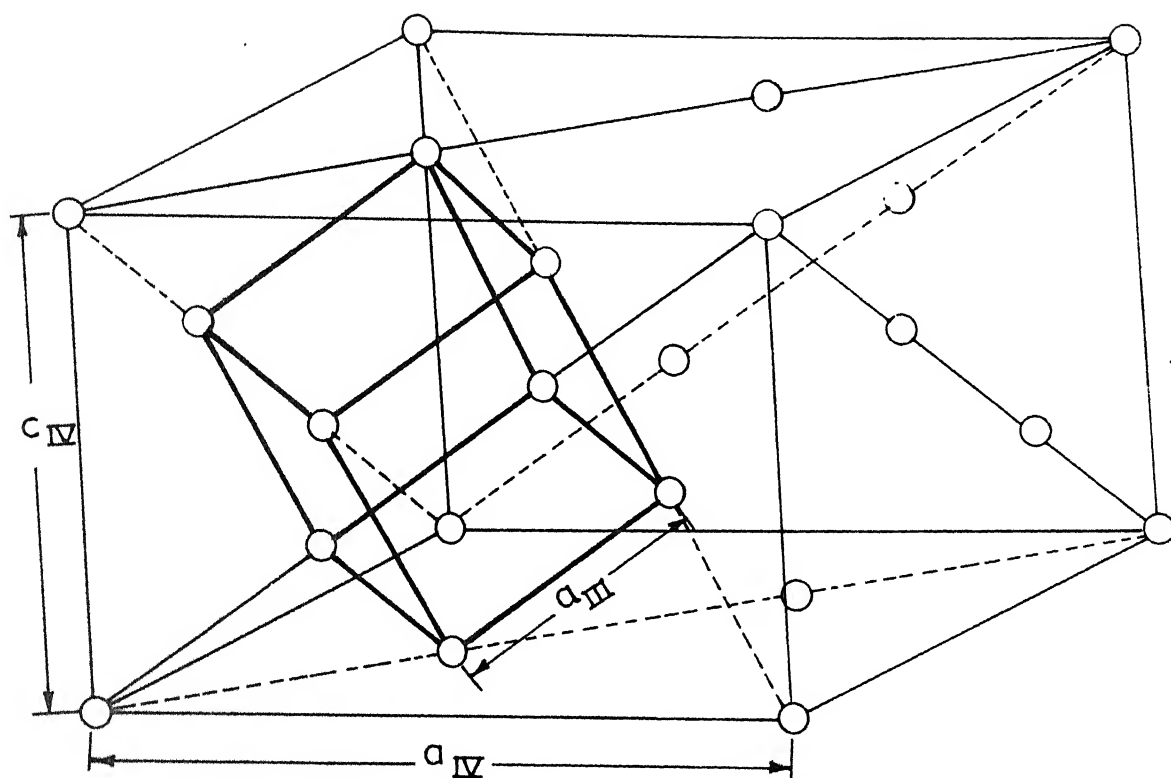


Fig. 5.7: Structural relationship between phases IV and III of  $\text{RbNO}_3$  [ref. 13].

where  $a_{IV}$ ,  $c_{IV}$  and  $a_{III}$  are the lattice parameters of the phases IV and III respectively.

From (1) and (2),

$$\begin{aligned} a_{IV} &= \sqrt{6} a_{III} \\ \text{and } c_{IV} &= \sqrt{3} a_{III} \\ a_{IV} &= \sqrt{2} c_{IV} \end{aligned} \quad (3)$$

As seen in section 1.2, Brown and McLaren<sup>(4)</sup> also

pointed out that the c-axis of the trigonal phase transforms to cubic  $[111]$  direction and  $[10.1]$  of the trigonal to cubic edge at IV  $\rightarrow$  III transformation. This relationship was shown in fig.

1.2. The relationships (3) also indicate that going from phase III to IV the hexagonal parameters  $a_{IV}$  and  $c_{IV}$  are obtained in the directions  $[211]$  and  $[111]$  respectively of the cube. This is shown in fig. 5.8

The relationships (3) are also apparent from the lattice parameter values, as follows:

$$\begin{aligned} a_{IV} &= 10.63\text{\AA}, & \sqrt{6} a_{III} &= 10.65\text{\AA} \\ c_{IV} &= 7.51\text{\AA}, & \sqrt{3} a_{III} &= 7.53\text{\AA} . \end{aligned}$$

The  $a_{IV}$  and  $c_{IV}$  values quoted above are at  $161^{\circ}\text{C}$  and  $a_{III}$  value at  $170^{\circ}\text{C}$

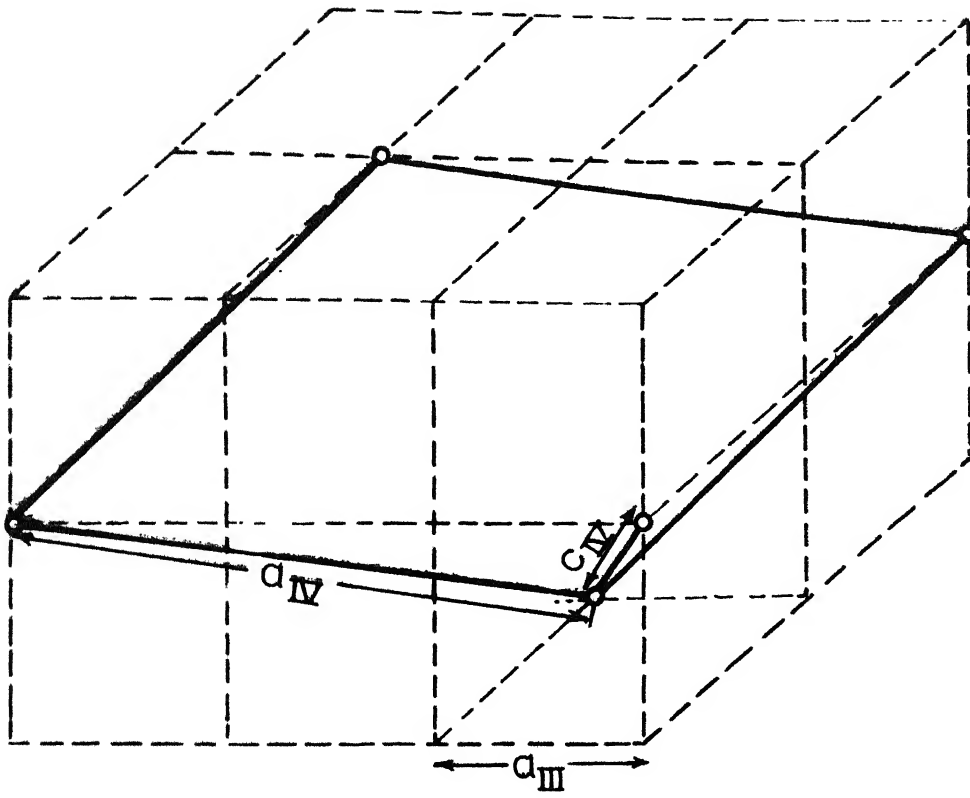


Fig. 5. Lattice relationship of phases III and IV in  $\text{RbNO}_3$ .

The volume of the trigonal phase IV can be written as

$$\begin{aligned} V_{IV} &= \frac{\sqrt{3}}{2} a_{IV}^2 c_{IV} \\ &= \frac{\sqrt{3}}{2} 6a_{III}^2 \sqrt{3} a_{III} \\ &= 9a_{III}^3 \end{aligned}$$

$$V_{IV} = 9V_{III} \quad (4)$$

This volume relationship between phases IV and III is consistent with the number of molecules per unit cell in these phases i.e.  $Z=9$  in phase IV and  $Z = 1$  in phase III.

5.2.3 III and II relation:

Phase II has been proposed by Brown and McLaren<sup>(4)</sup> as one of tetragonal symmetry. The simple relation between phases III and II was shown to be the following (see section 1.2):

$$\left. \begin{aligned} \sqrt{2} \quad a_{III} &= a_{II} \\ \text{and} \quad 2 \quad a_{III} &= c_{II} \end{aligned} \right\} \quad (5)$$

This is illustrated in fig. 1.3. The volume of phase II can be written as

$$\begin{aligned} V_{II} &= a_{II}^2 c_{II} \\ &= 2a_{III}^2 \cdot 2a_{III} = 4a_{III}^3 \end{aligned}$$

$$V_{IV} = 4V_{II} \quad (6)$$

This volume relationship is again consistent with the number of molecules per unit cell in each of these phases i.e.  $Z = 1$  for phase III and  $Z = 4$  for phase II.

As seen in section 5.2 a hexagonal (or rhombohedral) unit cell is a better choice for phase II. Hence it seems reasonable to propose that at III  $\rightarrow$  II transition the cube distorts to become a rhombohedron. The cubic edge ( $a_{\text{III}} = 4.38\text{\AA}$ ) of phase III gets elongated to become equal to the rhombohedral edge ( $a_{\text{II}}^{\text{R}} = 4.8\text{\AA}$ ) and the  $90^\circ$  angle of the cube changes to the rhombohedral angle ( $\alpha$ ) of  $70^\circ 48'$ . This is shown in fig. 5.9. This large expansion seems reasonable in view of the dilatometric observation at this phase transition. Also distortion of the cube angle is consistent with the bending and cracking of  $\text{RbNO}_3$  crystals observed by Brown and McLaren<sup>(4)</sup> at this phase change.

Since a rhombohedral cell has a corresponding hexagonal cell, we can write down the corresponding parameters for these two cells,

$$\begin{aligned} a_{\text{II}}^{\text{R}} &= 4.80\text{\AA}, & \text{and} & & a_{\text{II}}^{\text{hex}} &= 5.55\text{\AA} \\ \alpha^{\text{R}} &= 70^\circ 48' & & & c_{\text{II}}^{\text{hex}} &= 10.71\text{\AA} \end{aligned} \quad (7)$$

$$\begin{aligned} \text{Also (see below), } \sqrt[4]{2} a_{\text{III}} &= 5.21\text{\AA} \\ \text{and } \sqrt{6} a_{\text{III}} &= 10.73\text{\AA} \end{aligned} \quad (8)$$

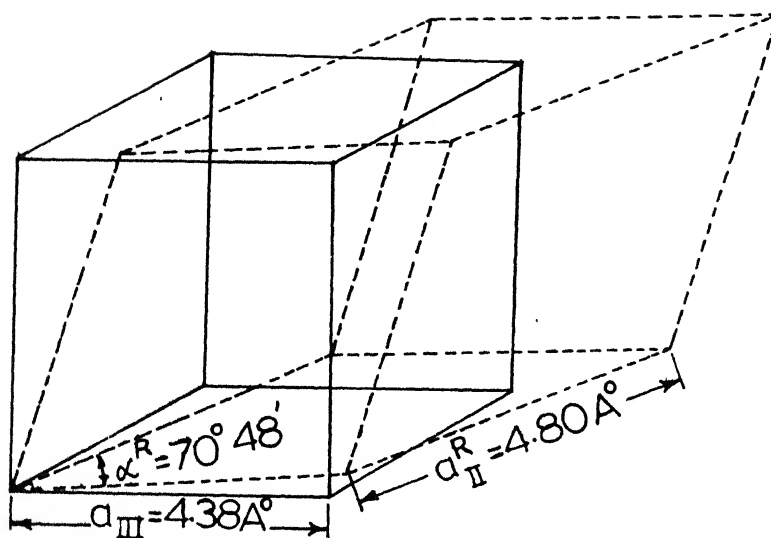


Fig. 5.9: Proposed structural <sup>\*</sup> relationship between the cubic phase III and the rhombohedral phase II.

The lattice parameters in eqn.(7) are taken at 227°C and in eqn.(8) at 222°C

Based on the equivalence of unit cell volumes of phases II and III, it can be shown that

$$\begin{aligned} a_{II}^{\text{hex}} &\approx \sqrt[4]{2} a_{II}^* \\ \text{and } c_{II}^{\text{hex}} &\approx \sqrt{6} a_{III} \end{aligned} \quad (9)$$

that the volume of phase II is

$$\begin{aligned} V_{II} &= \frac{\sqrt{3}}{2} a_{II}^{\text{hex}2} c_{II}^{\text{hex}} \\ &= \frac{\sqrt{3}}{2} \sqrt{2} a_{III}^2 \sqrt{6} a_{III} \\ &= 3a_{III}^3 \end{aligned}$$

$$V_{II} = 3V_{III} \quad (10)$$

This volume relationship, between phases III and II, agrees with the number of formula units in these phases i.e.  $Z = 1$  for phase III and  $Z = 3$  for phase II.

#### 5.2.4 II and I relation.

At 281°C, the rhombohedral parameters of phase II are

$$\begin{aligned} a_{II}^R &= 4.81 \text{ \AA} \\ \text{and } \alpha^R &= 69^\circ 8' \end{aligned} \quad (11)$$

The volume of phase II is

$$V_{II} = a_{II}^3 \sqrt{1 - 3\cos^2 \alpha^R + 2\cos^3 \alpha^R}$$

$$= 93.63 \text{ \AA}^3$$

Assuming that no change in volume took place at  $II \rightarrow I$  transition except that the rhombohedral angle changed from  $69^\circ 8'$  to  $60^\circ$ , the resulting rhombohedral edge will be  $5.07 \text{ \AA}$ . It may be noted that phase I has Sodium Chloride type structure. Joining the cube corners, at the end of a body diagonal, with the face centres yields a rhombohedron (fig. 5.10). If this rhombohedral edge ( $a_R$ , in phase II) becomes equal to half the face diagonal of a cube of phase I (fig. 5.10), then we can write down the cubic edge of phase I as,

$$\frac{\sqrt{2} a_I}{2} = 5.07$$

$$\text{or } a_I = 7.17 \text{ \AA}$$

This value of cubic edge is close to the observed value at  $290^\circ \text{C}$ , viz  $7.32 \text{ \AA}$ . The difference may be due to the large thermal expansion taking place at  $II \rightarrow I$  transition as is evident from fig. 4.15.

Since a rhombohedral cell has a corresponding hexagonal cell, the corresponding parameters may be written as



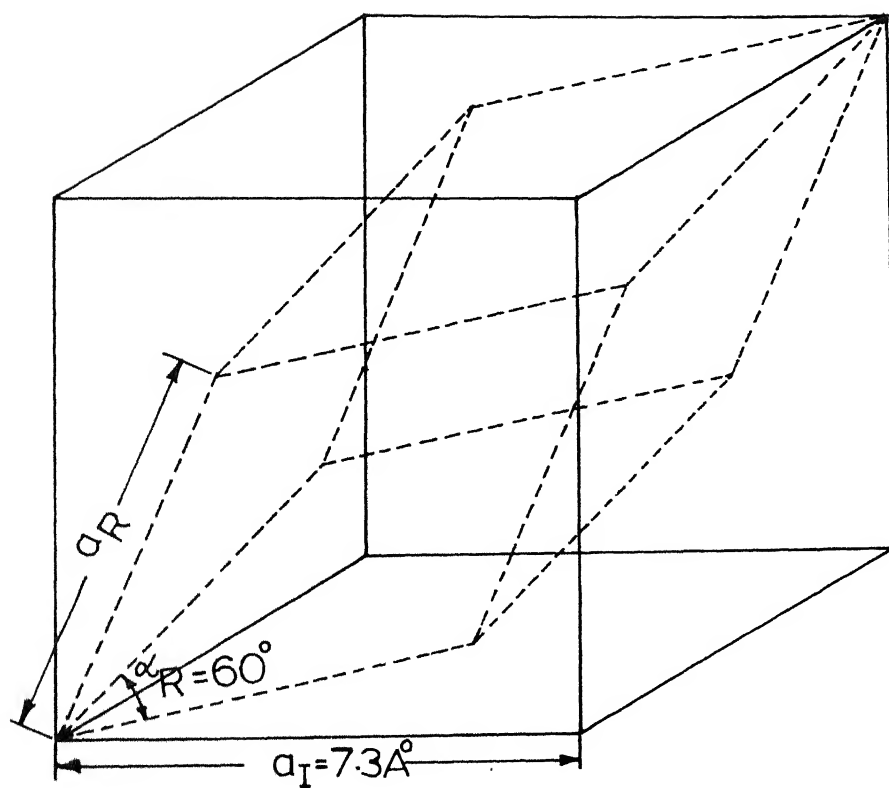


Fig. 5.10: Proposed structural relationship between the cubic phase I and the rhombohedral phase II.

$$\begin{aligned} a_{II}^{\text{hex}} &= 5.47 \text{Å}^0 & a_{II}^R &= 4.81 \text{Å}^0 \\ c_{II}^{\text{hex}} &= 10.89 \text{Å}^0 & \alpha^R &= 69^\circ \end{aligned} \quad (12)$$

From (12), we may also write

$$c_{II}^{\text{hex}} = 2a_{II}^{\text{hex}} \quad (13)$$

Also,

$$\begin{aligned} a_I &= 7.32 \text{Å}^0, & \sqrt[4]{3} a_{II}^{\text{hex}} &= 7.20 \text{Å}^0 \\ \frac{2}{3} c_{II}^{\text{hex}} &= 7.26 \text{Å}^0 \end{aligned}$$

Hence the lattice relationships may be

$$a_I \simeq \sqrt[4]{3} a_{II}^{\text{hex}} = \frac{2}{3} c_{II}^{\text{hex}} \quad (14)$$

These relationships can be derived from the equivalence of unit cell volumes of phases II and I.

The volume of phase II may be written as

$$\begin{aligned} V_{II} &= \sqrt{\frac{3}{2}} a_{II}^{\text{hex}^2} c_{II}^{\text{hex}} \\ &\simeq \sqrt{\frac{3}{2}} \frac{a_I^2}{\sqrt{3}} \frac{3}{2} a_I \\ &= \frac{3}{4} V_I \\ \text{or } \frac{V_{II}}{3} &= \frac{V_I}{4} \end{aligned} \quad (15)$$

This volume relationship is again agreeable with the number of formula units in phases II and I i.e.  $Z = 3$  for phase II

### 5.3 Solid Solution Effects.

#### 5.3.1 Effect of Ionic Size and Solubility Limits:

Lattice parameters vs composition for  $(\text{Cs}, \text{Rb})\text{NO}_3$  and  $(\text{K}, \text{Rb})\text{NO}_3$  systems at room temperature are shown in fig. 5.11. It can be seen that in  $(\text{Cs}, \text{Rb})\text{NO}_3$  system the 'a' parameter increases at a faster rate than the 'c' parameter. After the solubility limit is reached in phase IV both become constant. In  $(\text{K}, \text{Rb})\text{NO}_3$  system both 'c' and 'a' decrease with  $\text{K}^+$  concentration and become constant when the solubility limit is reached as expected. It is, therefore, concluded that addition of  $\text{Cs}^+$  increases the lattice volume and addition of  $\text{K}^+$  decreases it. This is consistent because of the size of  $\text{Rb}^+$  ion being intermediate between those of  $\text{Cs}^+$  and  $\text{K}^+$  ions. (The radii of  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  are respectively  $1.33\text{\AA}$ ,  $1.48\text{\AA}$  and  $1.68\text{\AA}$ ). Another conclusion is that the solubility limit of  $\text{CsNO}_3$  in  $\text{RbNO}_3$ , in phase IV, is much greater than that of  $\text{KNO}_3$  in  $\text{RbNO}_3$ . This is probably due to the similarity of the room temperature phases of  $\text{RbNO}_3$  and  $\text{CsNO}_3$  and incompatibility of the room temperature phase of  $\text{RbNO}_3$  with that of  $\text{KNO}_3$ . (see table 5.6).

It was seen in Chapter 4 that in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system there is a complete disappearance of phase II in the range  $0.25 < x < 0.30$  during heating and cooling. From table 5.6 it is clear that phase I

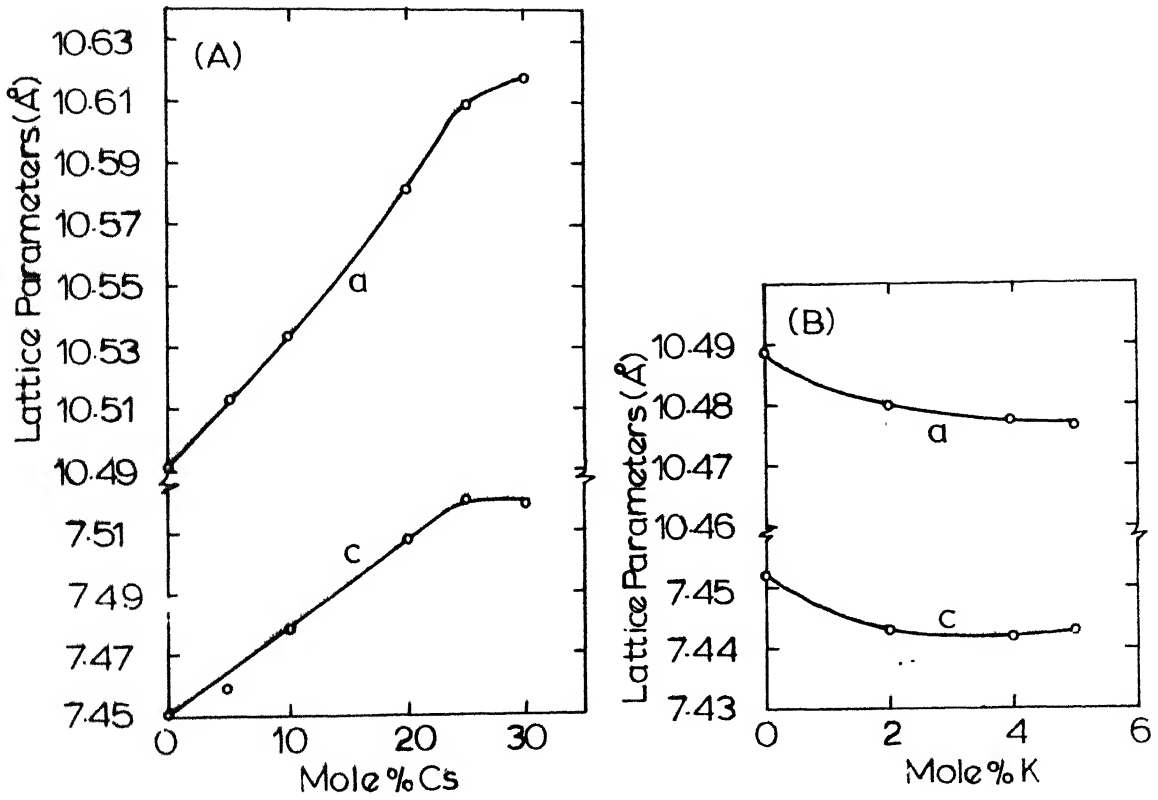


Fig. 5.11 Lattice parameters vs composition of (A)  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  and (B)  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  systems at room temperature.

TABLE: 5.6 Structural parameters of Nitrates of Rubidium, Cesium and Potassium in different phases.

Temperature (°C)	RbNO <sub>3</sub>	CsNO <sub>3</sub>	KNO <sub>3</sub>
0	Phase IV	Phase II <sup>(73)</sup>	Phase II <sup>(57)</sup>
	$a_H = 10.49^{\circ}$	$a_H = 10.87$	Orthorhombic $a = 5.41^{\circ}$
	$c_H = 7.44^{\circ}$	$c_H = 7.76$	$b = 9.14^{\circ}$
	$Z = 9$		$c = 6.43^{\circ}$
50	(Parameters at room temperature)		$Z = 4$
100			Phase III <sup>*</sup>
150			Phase I <sup>(75)</sup>
200	Phase III	Phase I <sup>(74)</sup>	$a_H = 5.385^{\circ}$
	$a = 4.36^{\circ}$	$a = 4.499^{\circ}$	$c_H = 9.760^{\circ}$
	$Z = 1$	(at 170°C)	$Z = 3$
	(at 190°C)		or
250	Phase II		$a_R = 4.50^{\circ}$
	$a_H = 5.54^{\circ}$		$\alpha_R = 73^{\circ} 30'$
	$c_H = 10.75^{\circ}$		$Z = 1$
	$Z = 3$		
	or $a_R = 4.80^{\circ}$ ,		
	$\alpha_R = 70^{\circ} 28'$		
	$Z = 1$ (at 232°C)		

TABLE 5.6 (Continued)

Temperature scale(°C)	RbNO <sub>3</sub>	CsNO <sub>3</sub>	KNO <sub>3</sub>
300	Phase I 7 52 <sup>o</sup> 4 (at 290 <sup>o</sup> C)		
	Liquid		
200			Liquid
100			
		Liquid	

The dotted lines represent the transformation temperatures.  
The arrows pointing up and down in the last column indicate  
cooling and heating respectively.

\* The lattice parameters of phase III (rhombohedral) of KNO<sub>3</sub>  
are  $a_R = 4.365 \text{ \AA}$ ,  $\alpha_R = 76^\circ 56'$  at 120°C (ref. 57).

of  $\text{CsNO}_3$  is similar to phase III of  $\text{RbNO}_3$ . This leads to an extension of phase III of  $\text{RbNO}_3$ , with increasing  $x$ , in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system at the expense of phase II. In  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system phase III disappears during cooling in the range  $0.03 < x < 0.05$ . Referring to table 5.6, it is evident that phase I of  $\text{KNO}_3$  is similar to phase II of  $\text{RbNO}_3$ . This results in the widening of phase II in  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system with increasing  $x$ .

It was noted in chapter 4 that the transformations in  $\text{RbNO}_3$  get smeared due to ionic substitutions in the two systems of solid solutions. This may be understood in terms of the distortion of the  $\text{RbNO}_3$  lattice due to these substitutions.  $\text{K}^+$  substitution seems to distort the lattice more than what  $\text{Cs}^+$  does.

### 5.3.2 Shifting of Transformation Temperatures.

As seen in chapter 4 the transformation temperatures of  $\text{RbNO}_3$  get shifted by partial substitution of  $\text{Rb}^+$  ions by ions of comparatively larger size e.g.  $\text{Cs}^+$  or of smaller size e.g.  $\text{K}^+$ . It was observed that transition temperature  $\text{III} \rightleftharpoons \text{II}$  shifts markedly towards higher or lower temperatures by ionic substitutions of  $\text{Rb}^+$  with  $\text{Cs}^+$  or  $\text{K}^+$  respectively. The transition temperatures  $\text{IV} \rightleftharpoons \text{III}$  and  $\text{II} \rightleftharpoons \text{I}$  are shifted slightly to lower temperatures in both types of substitution

This shifting of transition temperatures is explained below on the basis of (i) similarity of phases of  $\text{KNO}_3$  and  $\text{CsNO}_3$  with those of  $\text{RbNO}_3$  and (ii) activation energy values determined from the differential thermal analysis studies.

### 5.3.3 Similarity of Phases:

As seen in section 5.3.1 the phases IV and III of  $\text{RbNO}_3$  are similar to the phases II and I of  $\text{CsNO}_3$ . Also the transformation temperature  $\text{IV} \rightleftharpoons \text{III}$  in  $\text{RbNO}_3$  and  $\text{II} \rightleftharpoons \text{I}$  in  $\text{CsNO}_3$  are quite close (table 5.6). Due to these reasons the transformation temperature  $\text{IV} \rightleftharpoons \text{III}$  in  $\text{RbNO}_3$  is not much affected with increasing  $x$  in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$ . From table 5.6 it is seen that the temperature range of phase I of  $\text{CsNO}_3$ , which is similar to phase III of  $\text{RbNO}_3$ , is very large. Hence phase III extends in  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  system with increasing  $x$ . Since the only way it can extend is by shifting  $\text{III} \rightarrow \text{II}$  transition, therefore, this transition temperature shifts markedly to higher temperatures with concentration of  $\text{CsNO}_3$ .

It was seen in section 5.3.1 that phase II of  $\text{RbNO}_3$  is similar to phase I of  $\text{KNO}_3$ . Hence in  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  system, phase II becomes wider with increasing  $x$ . Since the transition temperature  $\text{II} \rightarrow \text{I}$  in  $\text{KNO}_3$  is very much lower than  $\text{IV} \rightarrow \text{III}$  in  $\text{RbNO}_3$  so that phase II in  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  has a tendency to extend on the low temperature



side. This results in a substantial shifting of  $\text{III} \rightleftharpoons \text{II}$  transition with increasing concentration of  $\text{KNO}_3$ .

#### 5.3.4 Thermal Activation Energy.

As seen in section 4.2 on "Thermodynamic parameters from DTI", the activation energy  $E_a$  is proportional to the slope of activation energy plot. In fig. 5.12 if straight line 1 represents the activation energy plot for the pure material then 2 and 3 represent those for the solid solutions  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  and  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  at  $\text{III} \rightarrow \text{II}$  transformation. It is seen from this figure that for the same rate constant (or rate of transformation) if the slope increases from curves 1 to 3 (and hence the activation energy also) the transformation temperature  $T$  increases and vice versa. If the value of rate constant is also slightly lowered then these changes of transformation temperature are even more. In  $\text{III} \rightarrow \text{II}$  transformation, the rate of transformation is lowered in both systems i.e.  $\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3$  and  $\text{K}_x\text{Rb}_{1-x}\text{NO}_3$  but  $E_a$  increases in the first system and decreases in the second system (Table 4.3). Therefore, transformation temperature increases and decreases respectively for these systems.

In  $\text{IV} \rightarrow \text{III}$  transformation the activation energy is lowered in both the systems (Table 4.3) and hence the transformation temperature in both cases is slightly lowered. These conclusions may be regarded as semiquantitative only.

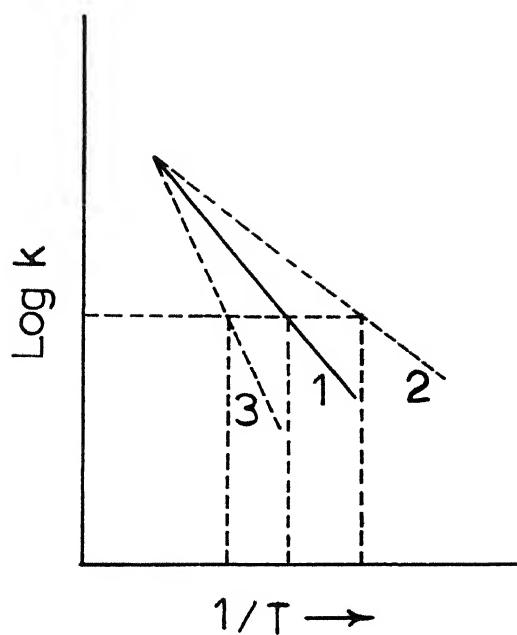


Fig. 5.12: Schematic diagram showing the effect of ionic substitution on the activation energy plot.

#### 5.4 Infrared Absorption:

The infrared absorption spectra of  $\text{RbNO}_3$ , from  $30^\circ\text{C}$  to  $294^\circ\text{C}$ , which is near its melting point, are presented in figs. 4.18 and 4.19 and of the solid solutions  $\text{Cs}_{0.10}\text{Rb}_{0.90}\text{NO}_3$  and  $\text{K}_{0.02}\text{Rb}_{0.98}\text{NO}_3$  at room temperature in figs. 4.21 and 4.22. Table 4.5 lists the fundamental modes of vibration of  $\text{NO}_3^-$  ion in different phases of  $\text{RbNO}_3$  and table 4.6 gives a comparative study of these modes in the solid solutions at room temperature. In this section we wish (i) to interpret the spectra in <sup>the</sup> four crystalline phases of  $\text{RbNO}_3$  and (ii) to explain the changes in infrared spectra of  $\text{RbNO}_3$  due to partial substitution of  $\text{Cs}^+$  and  $\text{K}^+$  for  $\text{Rb}^+$ .

The spectra of  $\text{RbNO}_3$  consist almost exclusively of the frequencies to be associated with the  $\text{NO}_3$  group<sup>(52)</sup>. Starting with the spectrum of a free nitrate ion, correlation charts giving the theoretical pattern of the spectrum of the nitrate ion in different phases can be set up.

A free nitrate ion belongs to the symmetry point group  $D_{3h}$  and has four distinct fundamental modes, as shown below (Table 5.7)<sup>(71)</sup>.

TABLE: 5.7 The spectral activity, approximate position, species and types of vibration of fundamental modes of  $\text{NO}_3^-$  ion of symmetry  $D_{3h}$ .

Fundamental mode	Species	Type of vibration	Approximate frequency ( $\text{cm}^{-1}$ )	Spectral activity
$\nu_1$	$A'_1$	Symmetric stretching	1050	Raman (R)
$\nu_2$	$A''_2$	Out-of-plane bending	830	Infrared (IR)
$\nu_3$	$E'$	degenerate-stretching	1390	(R, IR)
$\nu_4$	$E'$	degenerate-bending	720	(R, IR).

#### 5.4.1 Phase IV:

According to Pauling and Sherman<sup>(68)</sup> the room temperature phase of  $\text{RbNO}_3$  is hexagonal, space group  $C_{3v}^2$  with nine molecules per unit cell (fig. 5.14).

From fig. 5.14 it is evident that there are two sets of sites for  $\text{NO}_3$  group in the hexagonal structure, one set having site symmetry  $C_{3v}$  and the other set having site symmetry  $C_s$ . Let the co-ordinate axes be so chosen that the z-axis is perpendicular to the

plane of the  $\text{NO}_3^-$  ion (or plane of the paper) and x-axes coincides with one of the N-O bonds. The correlation table 5.8 shows that at this site all the modes become infrared active, the resulting modes entering into the various species of the group  $C_{3v}^2$  as shown

TABLE 5.8 Correlation showing the fundamental modes of  $\text{NO}_3^-$  ion (of site symmetry  $C_s$ ) entering into various species of the group  $C_{3v}^2$ .

Transition dipole component in $D_{3h}$ group.	Fundamental modes	Species of $D_{3h}$ symmetry	Species of $C_s$ symmetry	Species of $C_{3v}^2$ symmetry	Transition dipole components in $C_{3v}^2$ group.
$T_z$	$\nu_1$	$A_1'$	$A'$	$A_1'$	$T_z$
$T_x, T_y$	$\nu_2$	$A_2'$	$(T_x, T_y)$		
	$\nu_3, \nu_4$	$E$	$A''$	$E$	$T_x, T_y$
			$(T_z)$	$A_2$	

in this table. The selection rules for this group show that only the species  $A_1$  and  $E$  are infrared active with their transition dipoles along the z, and x,y directions respectively. Thus the modes  $\nu_1, \nu_2$ ,

$\nu_3$  and  $\nu_4$  will have two components each, which are infrared active.

Correlation table 5.9 gives the resulting species due to the site symmetry  $C_{3v}$ . The selection rules for this group, as already seen, show that the species  $A_1$  and E are infrared active. Therefore, the

TABLE 5.9 Correlation showing the fundamental modes of  $NO_3$  group, of site symmetry  $C_{3v}$ , entering into the various species of the  $C_{3v}$  group.

Transition dipole compo- nents in $D_{3h}$ sym group	Funda- mental modes	Species of $D_{3h}$ symmetry	Species of $C_{3v}$ symmetry	Transition dipole compo- nents in $C_{3v}$ group.
	$\nu_1$	$A_1'$		
$T_z$	$\nu_2$	$A_2''$	} $A_1$	$T_z$
$T_x, T_y$	$\nu_3, \nu_4$	$E'$	E	$T_x, T_y$

modes  $\nu_1, \nu_2, \nu_3$  and  $\nu_4$  will have one component each. Both sets of sites contribute to the transition dipoles. To understand the observed number of components the following explanation seems reasonable. Consider fig. 5.13. The symbols  $IA_1$ ,  $IE$  and  $IIA_1$ ,  $IIE$

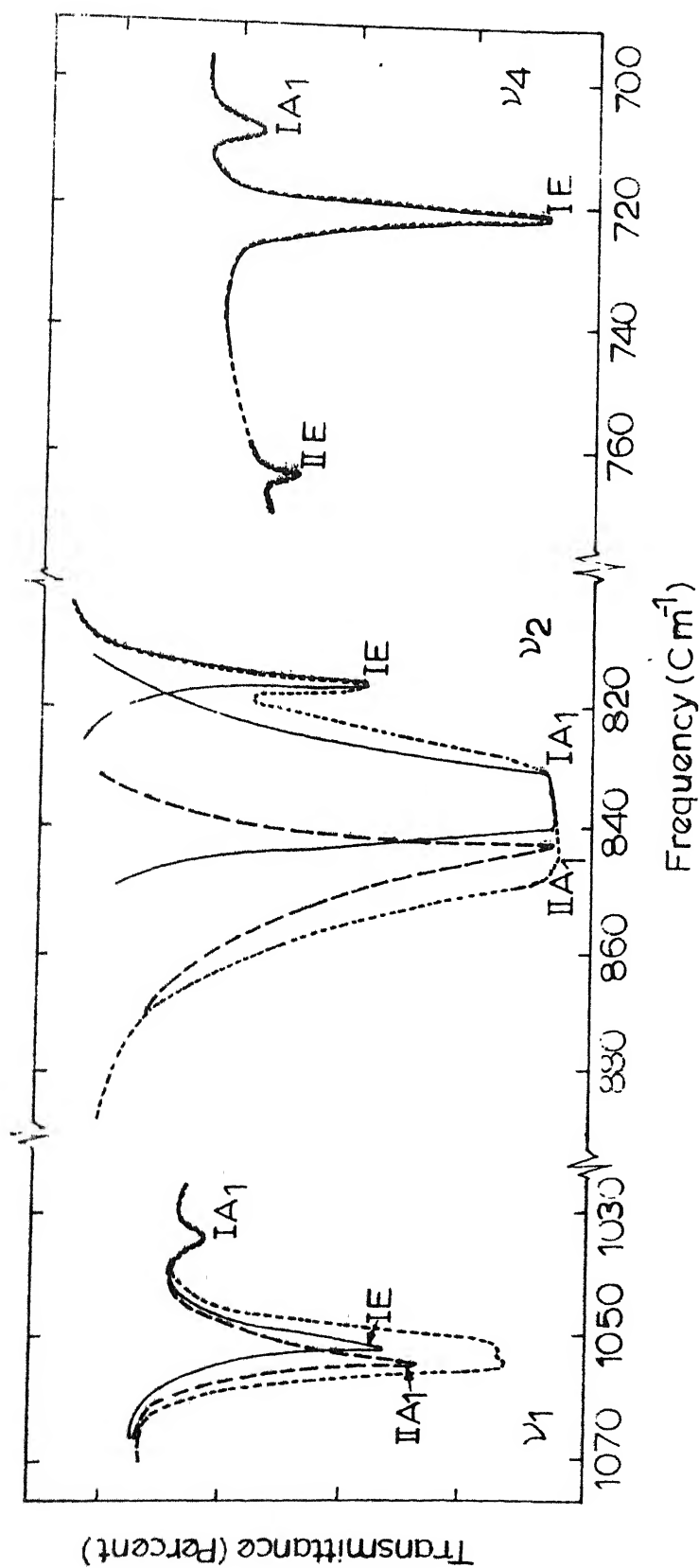


Fig. 5.13: Schematic diagram showing the number of components observed in phase IV of RbNO<sub>3</sub>. Curves shown by smaller dashes are the observed traces, continuous curves are due to sites of set I and those shown by longer dashes are due to sites of set II. A<sub>1</sub> and E represent the symmetry species.

represent the different species ( $A_1$  or E) preceded by the number of set (i.e. I or II) of sites. Let the continuous curves show the absorption peaks due to the set I (of site symmetry  $C_s$ ) and curves, shown by longer dashes, due to the set II (of site symmetry  $C_{3v}$ ), then the curves shown by smaller dashes, which are the resultant of these (i.e. the continuous and (longer) dashed curves), represent the observed absorption peaks. It may be noted that the components due to the site symmetry  $C_{3v}$  (set II) lie at higher frequencies as compared to those due to site symmetry  $C_s$ . This is probably because the  $NO_3$  groups with lower site symmetry ( $C_s$ ) are perturbed more by the environmental symmetry than the sites of symmetry  $C_{3v}$ . The latter site symmetry is the same as the environmental symmetry and is therefore, less perturbed. Due to this difference in perturbation the vibrations of set I are damped more than those of set II. Hence vibrational frequencies of set I occur at lower frequencies as compared to those of set II. This effect is expected to be least in the case of symmetrical stretching vibration  $\nu_1$ , a little more for the out-of-plane bending mode  $\nu_2$  and maximum for  $\nu_3$  and  $\nu_4$  modes. It may be pointed out that the z-components of the modes  $\nu_1$ ,  $\nu_3$  and  $\nu_4$  which are derived from the in-plane vibration modes of the nitrate ion, are expected to be weaker than the x and y



components. Similarly the x and y components of the mode  $\nu_2$ ,

derived from the out-of-plane bending vibration mode, should be weaker than the z-component.

It is clear from fig 5.13 that three bands at  $708\text{ cm}^{-1}$ ,  $722\text{ cm}^{-1}$  and  $764.5\text{ cm}^{-1}$  can be assigned to the three components of  $\nu_4$  (two due to sites of set I and one due to sites of set II).

Their individual assignment may be E  $722\text{ cm}^{-1}$  and  $A_1\ 708\text{ cm}^{-1}$  due to sites of set I and  $A_1\ 764.5\text{ cm}^{-1}$  due to sites of set II (fig.5.13).

A broad band centered around  $838\text{ cm}^{-1}$  corresponds to  $\nu_2$  mode and has two components due to sites of set I. Individual assignment may be  $838\text{ cm}^{-1}(A_1)$  and  $816.5\text{ cm}^{-1}(E)$  due to set I and  $A_1(845\text{ cm}^{-1})$  due to set II (fig 5.13). Two bands at  $1056\text{ cm}^{-1}$  and  $1036\text{ cm}^{-1}$  (fig.5.13) are observed in the region of symmetric stretching mode  $\nu_1$ . The stronger one at  $1054\text{ cm}^{-1}$  may be assigned to E and weaker at  $1036\text{ cm}^{-1}$  to  $A_1$  species due to sites of set I and the other at  $1056\text{ cm}^{-1}$  of species  $A_1$  due sites of set II (fig 5.13) It is not clear why the inactive mode  $\nu_1$  gives rise to two components  $A_1$  and E in phase IV.

The absorption in the region of  $\nu_3$  is too broad to give any information and has, therefore, not been studied.

It may be remarked that Brown and McLaren<sup>(4)</sup> have given a space group  $D_3^4$  or  $D_3^6$  for phase IV of  $\text{RbNO}_3$ . If correlation chart

is prepared by taking  $D_3^4$  or  $D_3^6$  as the symmetry group then the number of components of vibrational modes of  $\text{NO}_3^-$  ion do not correspond to what is observed in the present spectra.

As seen above, the occurrence of more than one absorption peak for the modes  $\nu_1$ ,  $\nu_2$  and  $\nu_4$ , is explained on the basis of the inequivalence of two sets of sites of  $\text{NO}_3^-$  ion in phase IV. It may be noted that this is only one of the possible explanations. Another explanation which also appears to be reasonable is that the weak additional components observed are mostly due to natural abundant isotopic species of  $\text{NO}_3^-$  ion involving either a  $^{15}\text{N}$  atom or an  $^{18}\text{O}$  atom. The natural abundances of  $^{15}\text{N}$   $^{16}\text{O}_3^-$  and  $^{14}\text{N}$   $^{16}\text{O}_2$   $^{18}\text{O}^-$  are 0.36 percent and 0.61 percent while each of the other isotopic combination involving  $^{15}\text{N}$  or  $^{18}\text{O}$  has only less than 0.002 percent abundance. Thus one may expect weak absorption, due to  $^{14}\text{N}$   $^{16}\text{O}_2$   $^{18}\text{O}^-$  and  $^{15}\text{N}$   $^{16}\text{O}_3^-$  isotopic species in addition to the strong absorption due to the main species  $^{14}\text{N}$   $^{16}\text{O}_3^-$ .

Kato and Rolfe<sup>(76)</sup> have recently studied the absorptions due to naturally abundant isotopic species and enriched isotopic species of  $\text{NO}_3^-$  ion in KBr with different varieties of combinations of  $^{15}\text{N}$ ,  $^{14}\text{N}$ ,  $^{16}\text{O}$  and  $^{18}\text{O}$ . We will restrict ourselves here with the species  $^{14}\text{N}$   $^{16}\text{O}_3^-$ ,  $^{15}\text{N}$   $^{16}\text{O}_3^-$  and  $^{14}\text{N}$   $^{16}\text{O}_2$   $^{18}\text{O}^-$  as we are only

interested in molecules with sufficient natural abundance to show up in absorption. All the four modes of vibration of  $\text{NO}_3^-$  ion (i.e.  $\nu_1, \nu_2, \nu_3$  and  $\nu_4$ ) have been observed for  $\text{NO}_3^-$  ion in KBr where the symmetry was assumed to be  $D_{3h}$  though  $\nu_1$  is expected to be inactive in the infrared. The  $\nu_3$  and  $\nu_4$  of  $\text{NO}_3^-$  ion with  $D_{3h}$  or  $C_{3v}$  symmetry will split into two ( $A_1, B_1$ ) for species like  $^{14}\text{N} \ ^{16}\text{O}_2 \ ^{18}\text{O}^-$  which have a site symmetry of  $C_{2v}$ . The observed and calculated positions for  $\nu_1, \nu_2, \nu_3$  and  $\nu_4$  for the different isotopic species of  $^{14}\text{N} \ ^{16}\text{O}_3^-$ ,  $^{15}\text{N} \ ^{16}\text{O}_3^-$  and  $^{14}\text{N} \ ^{16}\text{O}_2 \ ^{18}\text{O}^-$  according to the Kato and Rolfe<sup>(76)</sup> are given in table 5.10.

The  $\nu_3$  vibration is too strong and broad and its components are unobservable. The assignments of the various absorption peaks corresponding to  $\nu_1, \nu_2$  or  $\nu_4$  observed at room temperature (or phase IV) in the present study of  $\text{RbNO}_3$  are given in table 5.11. The assignments here for  $\text{NO}_3^-$  ion in  $\text{RbNO}_3$  are based on the assignments of  $\text{NO}_3^-$  ion in KBr of table 5.10.

It may be noted that all the observed peaks except the one at  $762\text{cm}^{-1}$  could be very well explained as belonging to the naturally abundant isotopic species of  $\text{NO}_3^-$  ion.

To have a better understanding of the components it may probably be worth while to study the infrared and Raman spectra of

single crystals of  $\text{RbNO}_3$  at different temperatures (at low as well as high temperatures).

TABLE 5.10<sup>(76)</sup>. Experimental and calculated values of the vibrational frequencies of  $^{14}\text{N}^{16}\text{O}_3^-$ ,  $^{15}\text{N}^{16}\text{O}_3^-$  and  $^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-$  ions in KBr

$\nu(\text{cm}^{-1})$		Vibrational mode	Molecule
Experimental	Calculated		
1383.2	1383.3	$\nu_3(\text{E})$	$^{14}\text{N}^{16}\text{O}_3^-$
1383.2	1381.9	$\nu_3(\text{B}_2)$	$^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-$
1371.1	1371.3	$\nu_3(\text{A}_1)$	$^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-$
1352.3	1349.1	$\nu_3(\text{E})$	$^{15}\text{N}^{16}\text{O}_3^-$
1054.8	1054.3	$\nu_1(\text{A}_1)$	$^{14}\text{N}^{16}\text{O}_3^-$
1055.1	1054.8	$\nu_1(\text{A}_1)$	$^{15}\text{N}^{16}\text{O}_3^-$
1034.9	1034.8	$\nu_1(\text{A}_1)$	$^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-$
841.3	841.4	$\nu_2(\text{A}_2)$	$^{14}\text{N}^{16}\text{O}_3^-$
837.8	837.8	$\nu_2(\text{B}_1)$	$^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-$
820.0	819.4	$\nu_2(\text{A}_2)$	$^{15}\text{N}^{16}\text{O}_3^-$
715.6	715.7	$\nu_4(\text{E})$	$^{14}\text{N}^{16}\text{O}_3^-$
714.4	714.5	$\nu_4(\text{E})$	$^{15}\text{N}^{16}\text{O}_3^-$
	704.8	$\nu_4(\text{A}_1)$	$^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-$
	692.5	$\nu_2(\text{B}_2)$	$^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-$

TABLE 5.11 Assignments of the observed absorptions in  $\text{RbNO}_3$  in phase IV to vibrational modes of  $^{14}\text{N}^{16}\text{O}_3^-$ ,  $^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-$  and  $^{15}\text{N}^{16}\text{O}_3^-$ .

Observed $\nu$ ( $\text{cm}^{-1}$ )	Assignment	Molecule
1056 <sup>a</sup>	$\nu_1$	$^{15}\text{N}^{16}\text{O}_3^-$
1054 <sup>a</sup>	$\nu_1$	$^{14}\text{N}^{16}\text{O}_3^-$
1035.5	$\nu_1$	$^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-$
838 <sup>b</sup>	$\nu_2$	$^{14}\text{N}^{16}\text{O}_3^-$
816.5 <sup>b</sup>	$\nu_2$	$^{15}\text{N}^{16}\text{O}_3^-$
764.5	$\nu_4$	
722	$\nu_4$	$^{14}\text{N}^{16}\text{O}_3^-$
708	$\nu_4$	$^{14}\text{N}^{16}\text{O}_2^{18}\text{O}^-$

<sup>a</sup> The weak absorption at  $1056 \text{ cm}^{-1}$  probably overlaps with strong absorption of  $1054 \text{ cm}^{-1}$ , so that one sees the appearance of a barely resolved doublet.

<sup>b</sup> The weak absorption at  $816.5$  partly overlaps the strong and broad band at  $838 \text{ cm}^{-1}$ .

As the temperature is raised in this phase the intensity of the fundamental modes of vibration is reduced. This is evident from Figs. 4.18 to 4.20

From the shape of the bands on either side of the absorption peak  $\nu_1$  (figs. 4.19 and 4.22) it seems that these are similar to the P and R branches in the rotation-vibration spectra<sup>(70)</sup>.

This means that associated with the vibrational modes of  $\text{NO}_3$  group is some amount of rotation about the trigonal axis. The rotational components of absorption band may be too close to be resolved in the present case. This can be seen from the following considerations.

The rotational constant of  $\text{BF}_3$  molecule in its ground state are<sup>(72)</sup>  $B_{[O]} = 0.35 \text{ cm}^{-1}$  and  $A_{[O]} = 0.17 \text{ cm}^{-1}$ . The molecule  $\text{BF}_3$  has a plane symmetrical form similar to the  $\text{NO}_3$  group. The atomic weights of F and O are 19 and 16 respectively. The bond lengths N-O and B-F are<sup>(71)</sup>  $1.22 \text{ \AA}$  and  $1.29 \text{ \AA}$  respectively. The ratio of moments of inertia  $\left[ \frac{I_B}{I_A} = \frac{3}{2} \frac{m r^2}{m r^2} \right]$  of  $\text{NO}_3$  and  $\text{BF}_3$  is 0.89. The corresponding rotational constants of  $\text{NO}_3$  group will, therefore, be  $B_{[O]} = 0.4 \text{ cm}^{-1}$  and  $A_{[O]} = 0.2 \text{ cm}^{-1}$ . Hence separation of the rotational components in the band will be less than  $1 \text{ cm}^{-1}$ .

It may be remarked that if single crystals of  $\text{RbNO}_3$  and high resolution instruments are used then it might be possible

to resolve these components.

#### 5.4.2 Phase III

On heating to temperatures between  $164^{\circ}\text{C}$  and  $220^{\circ}\text{C}$   $\text{RbNO}_3$  transforms into a cubic phase. The space group reported by Korhonen<sup>(11)</sup> is  $T_h^6$  with four molecules per unit cell. The site symmetry is  $C_3^{(7)}$ . The correlation table 5.12 shows that at this site all the modes become infrared active, the resulting modes

TABLE 5.12 Correlation showing the fundamental modes of  $\text{NO}_3^-$  ion  
(of site symmetry  $C_3$ ) entering into various species  
of the group  $T_h^6$ .

Transition dipole compo- nent in $D_{3h}$ group.	Funda- mental sym. modes	Species of $D_{3h}$ sym.	Species of $C_3$ sym. (comps. of transition dipole)	Species of $T_h^6$ sym.	Transition dipole comps. in $T_h$ group.
$T_z$	$\nu_1$ $\nu_2$	$A_1'$ $A_2''$	$A$ ( $T_z$ )	$A'$ $A''$	
$T_x, T_y$	$\nu_3, \nu_4$	$E'$	$E$ ( $T_x, T_y$ )	$E'$ $E''$	$T$

in the group  $T_h^6$  are shown in this table. The selection rules for  $T_h^6$  group show that only the triply degenerate species  $F''$  is infrared active. Thus the modes  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  have one component each which is triply degenerate and is infrared active.

It is clear from figs 4.18 and 4.19 that only one component at  $200^\circ\text{C}$  i.e. in the cubic phase III is observed in each of the cases. The components due to sites of set II in phase IV in each of the modes  $\nu_1$ ,  $\nu_2$ , and  $\nu_4$  seem to have disappeared and the remaining two components due to site I in phase IV seem to have combined to give rise to one triply degenerate component in each case. This is probably due to the reduction in the sets of sites from two to one as we go from phase IV to III.

It is seen from fig. 4.20 that as the temperature is raised in phase III the fundamental modes  $\nu_1$ ,  $\nu_2$  and  $\nu_4$  go on diminishing in intensity. At  $207^\circ\text{C}$  their intensity has gone down so much that to observe them in this phase the reference beam in the double-beam spectrophotometer has to be attenuated using Perkin Elmer attenuator attachment. By referring to table 4.5 we can see that in phase IV as the temperature is raised from room temperature to  $100^\circ\text{C}$  the frequencies  $\nu_1$ ,  $\nu_2$  and  $\nu_4$  change by a maximum of  $1\text{ cm}^{-1}$  whereas at  $200^\circ\text{C}$  i.e. in going to phase III the change is  $3\text{ cm}^{-1}$  to



$5.5 \text{ cm}^{-1}$ . This comparatively large change in frequencies may be attributed to the phase transformation  $\text{IV} \rightarrow \text{III}$  which involves a sudden increase in volume at the phase change and hence weakening of the molecular bonds. Also at the phase change a slight increase in intensity of the fundamental absorptions is observed. This may also be understood on the basis of volume expansion at the phase transition. The amplitude of vibrations of the  $\text{NO}_3^-$  ion could increase, thus enhancing the intensity of the infrared absorption.

#### 5.4.3 Phase II.

As the temperature is raised above  $220^\circ\text{C}$  phase II appears. As already pointed out, the absorption bands became too weak to be observed without attenuation at temperatures above  $207^\circ\text{C}$ . Therefore, infrared spectra in phase II at different constant temperatures in the range  $230^\circ\text{C}$  upto  $280^\circ\text{C}$  have been obtained using the techniques described by Greenberg and Hallgren<sup>(52)</sup> as well as by suitable attenuation of the reference beam (section 4.5).

It is evident from figs. 4.18 and 4.19 that no fundamental absorption peaks are seen at  $230^\circ\text{C}$  and  $275^\circ\text{C}$  i.e. in phase II. This shows that the fundamental modes of vibration vanish in phase II. This may be discussed as follows.

Brown and McLaren<sup>(4)</sup> have proposed that  $\text{RbNO}_3$  exists in the tetragonal symmetry in phase II above  $220^\circ\text{C}$ . The space group of this phase is not known. However, the point groups  $C_4$ ,  $C_{4h}$ ,  $D_4$  and  $D_{2d}$  of the tetragonal system may be taken as the possible symmetry groups for phase II. In order that these possible point groups are realized in phase II the requirement of  $C_4$  axis of symmetry in  $C_4$ ,  $C_{4h}$  and  $D_4$  point groups and of  $S_4$  in point group  $D_{2d}$  requires a change in the position and orientation of  $\text{NO}_3^-$  planes. A possible model based on such orientational effects may be used to explain (1) - sharp decrease in electrical conductivity at the  $\text{III} \rightarrow \text{II}$  transformation, and (2) the difference in the thermal expansion measured by dilatometric and X-ray methods. This may be further supported by the observation of Kennedy<sup>(5)</sup> that after  $\text{III} \rightarrow \text{II}$  transformation recrystallization of  $\text{RbNO}_3$  takes place in phase II. Now the symmetry species of  $D_{3h}$  symmetry of the  $\text{NO}_3^-$  ion do not reduce to any of those in the tetragonal point groups cited above. The reason for this is that the common symmetry elements are no more than the identity. Hence no spectrum is observed in this phase.

As seen in section 5.2, a hexagonal (or rhombohedral) symmetry seems more probable for phase II. However, in the absence of detailed structural analysis of this phase, it is not possible to

analyse the infrared spectrum in this phase.

#### 5.4.4 Phase I:

When  $\text{RbNO}_3$  is heated above  $285^\circ\text{C}$  phase I appears. It has cubic symmetry but no structural determination has been reported so far.

Figs 4.18 and 4.19 (at  $294^\circ\text{C}$ ) show that the absorption bands at fundamental frequencies reappear. Greenberg and Hallgren<sup>(52)</sup> have also observed the infrared spectrum of  $\text{RbNO}_3$  at  $25^\circ\text{C}$  less than the melting point of  $\text{RbNO}_3$  (m.p. =  $310^\circ\text{C}$ ). The present observation shows that their spectrum is in cubic phase I.

Whereas no spectrum could be observed in phase II, a spectrum could be recorded on heating to higher temperatures to obtain phase I. This appears to indicate a gradual disordering of the  $\text{NO}_3$  groups due to the phase transformation. Such a picture is consistent with the gradual increase in electrical conductivity at the  $\text{II} \rightarrow \text{I}$  transition.

The frequencies observed in the spectrum of phase I are near the ones in the room temperature spectrum, suggesting that the fundamental frequencies of the  $\text{NO}_3$  group persist in phase I. A more detailed analysis of the infrared spectrum of phase I, however, has to await a determination of the structure of the cubic phase.

#### 5.4.5 Liquid Phase:

Greenberg and Hallgren<sup>(52)</sup> have also observed the infrared spectrum of  $\text{RbNO}_3$  in liquid phase ( $25^\circ\text{C}$  above the melting point).

This spectrum was found to be essentially similar to the one of phase I, indicating that in both cases the fundamental frequencies of the  $\text{NO}_3$  groups are the ones being observed.

#### 5.4.6 Solid Solutions:

In the solid solutions the spectra at room temperature (Figs. 4.21 and 4.22) show that  $\nu_1$ ,  $\nu_2$  and  $\nu_4$  frequencies shift to lower frequencies with  $\text{Cs}^+$  impurity (larger cation size) and to higher frequencies with  $\text{K}^+$  impurity (smaller cation size). As already referred to, Greenberg and Hallgren<sup>(52)</sup> in their study of infrared spectra of alkali metal nitrates have observed a similar shifting of  $\nu_1$  and  $\nu_4$  frequencies but the opposite behaviour for the mode  $\nu_2$ . The shifts in fundamental frequencies (table 4.6) observed by substituting  $\text{Cs}^+$  or  $\text{K}^+$  for  $\text{Rb}^+$  are very small. Therefore it is not possible to verify the conclusions of Greenberg and Hallgren<sup>(52)</sup> by the present study which involves partial substitution of cations whereas Greenberg and Hallgren<sup>(52)</sup> study is about the complete substitution of cations.

Also in general the intensities of absorption peaks of fundamentals reduce by  $\text{Cs}^+$  substitution and get enhanced during  $\text{K}^+$

substitution (figs. 4.21 and 4.22). This may be understood as follows. Substitution of the smaller  $K^+$  ion for  $Rb^+$  ion provides more available space for  $NO_3^-$  ion in the lattice and hence increases the amplitude of vibration of  $NO_3^-$  ion which leads to an increase in the intensity of the fundamentals of  $NO_3$  group. The reverse should be expected in case of substitution of larger  $Cs^+$  for  $Rb^+$ .

It may also be seen in fig. 4.22 that the low frequency component, of split components of E species, is more prominent in  $RbNO_3$  as compared to the other at higher frequency. The prominence of the low frequency component is enhanced by  $Cs^+$  substitution whereas it is reduced by  $K^+$  substitution. Instead, the component at higher frequency becomes more prominent in the  $K^+$  substitution.

The modes of vibration of  $NO_3^-$  ion in the solid solutions change with temperature in different phases in a manner similar to  $RbNO_3$ . They have been studied but not presented here.

## 5.5 Electrical Conductivity Changes and Mechanisms of Phase Transformations in $RbNO_3$ .

### 5.5.1: Electrical Conductivity Changes at Phase Transitions in $RbNO_3$ .

It was seen in section 1.3 (fig 1.4) that, from the conductance measurements on powder pellets of  $RbNO_3$ , Brown and McLaren<sup>(4)</sup> made the following observation: The transformation IV  $\rightarrow$  III

increases the conductivity of  $\text{RbNO}_3$  by a factor of about 100 and  $\text{III} \rightarrow \text{II}$  transition decreases it by a factor of 3. After completing  $\text{III} \rightarrow \text{II}$  transformation (for the first time), if the sample is cooled,  $\text{III} \rightleftharpoons \text{II}$  transformation involves a change of conductivity by a factor of 30 and  $\text{IV} \rightleftharpoons \text{III}$  transformation by a factor of 1000. These latter changes in conductivity are repeatable after traversing  $\text{III} \rightarrow \text{II}$  transformation for the first time (earlier changes in conductivity being no more observable). This permanent increase in the conductivity of phase III after first undergoing  $\text{III} \rightarrow \text{II}$  transition, however, remained unexplained.

In the present experiments a conductivity change by a factor of 100 at  $\text{IV} \rightleftharpoons \text{III}$  transition and by a factor of 3 at  $\text{III} \rightleftharpoons \text{II}$  transformation was never observed, as seen in the lower most graph of figs. 4.1 and 4.2. This suggests that, in the powder pellets of Brown and McLaren<sup>(4)</sup>, some recrystallization took place after traversing  $\text{III} \rightarrow \text{II}$  transformation. This was not the situation when the first change of conductivity, by a factor of 100 at  $\text{IV} \rightleftharpoons \text{III}$  transformation and by a factor of 3 at  $\text{III} \rightarrow \text{II}$  transition, was observed. Recrystallization of phase II, after  $\text{III} \rightarrow \text{II}$  transformation, has been recently reported by Kennedy<sup>(5)</sup>. Therefore, no such discrepancy in conductivity change at  $\text{IV} \rightleftharpoons \text{III}$  transformation was observable, when

samples of the present study were prepared, as already explained.

### 5.5.2 Mechanisms of Phase Transformations in $\text{RbNO}_3$ .

A brief discussion of the mechanisms of phase transformations in  $\text{RbNO}_3$  may be given in the light of the present study and the available literature on phase transitions of  $\text{RbNO}_3$ .

### 5.5.3 $\text{IV} \rightarrow \text{III}$ Transformation:

The hexagonal structure for the room temperature phase of  $\text{RbNO}_3$ , reported by Pauling and Sherman<sup>(68)</sup>, is reproduced in fig. 5.14. From this figure it is evident that the  $\text{NO}_3$  group has two sets of sites (or orientations). Two thirds of the  $\text{NO}_3^-$  ions have symmetry  $C_6$  (which could remove the possibility of disorder) and the remaining third have a symmetry  $C_{3v}$ <sup>(49)</sup>. Fig. 5.15 is drawn, following Berthoulet<sup>(11)</sup>, for the cubic structure of phase III. In this figure it can be seen that there are four equivalent orientations of symmetry  $C_{3v}$  available to the  $\text{NO}_3$  groups in the unit cell. During the transformation  $\text{IV} \rightarrow \text{III}$  the symmetry of all orientations increases to  $C_{3v}$  leading to disorder. This means that phase III is disordered with respect to phase IV in terms of the orientations of the  $\text{NO}_3$  groups.

The orientational disordering of  $\text{NO}_3$  group in phase III may be partly responsible for the increase in electrical conductivity at  $\text{IV} \rightarrow \text{III}$  transformation in  $\text{RbNO}_3$ . The increase in electrical

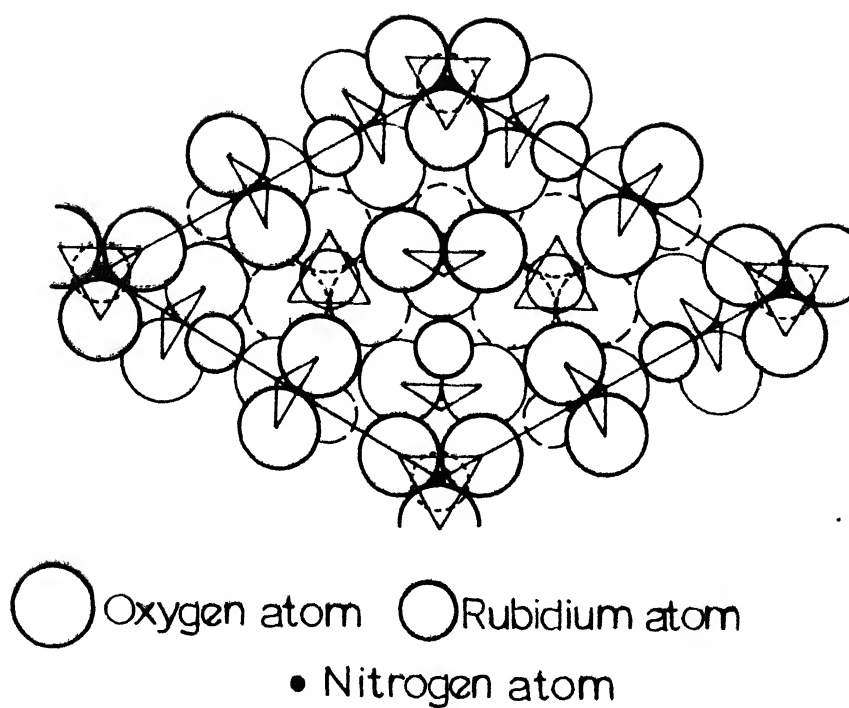
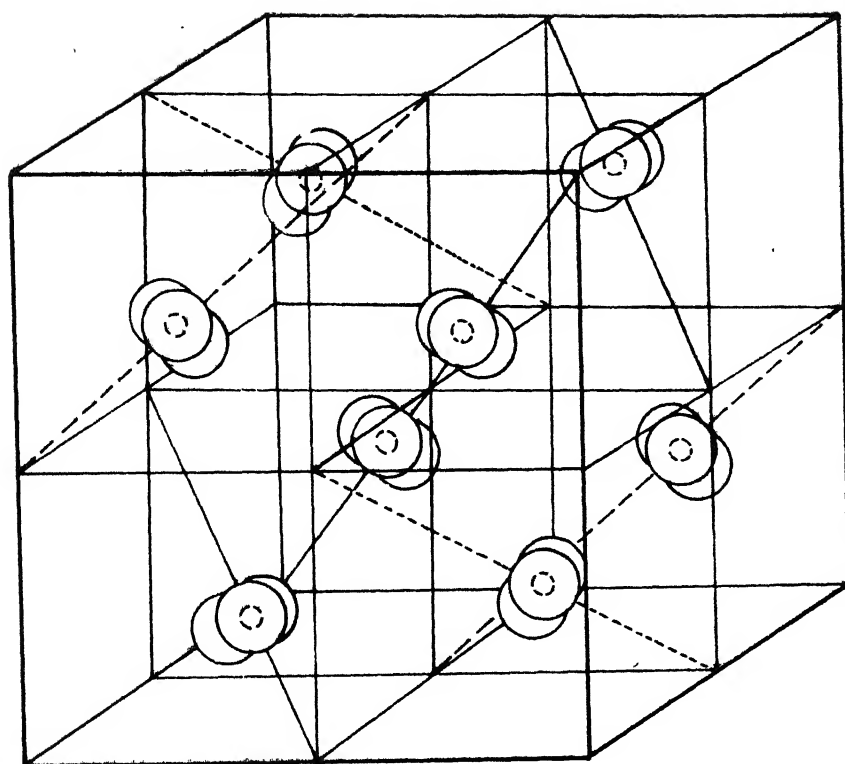


Fig. 5.14 Hexagonal crystal structure of phase IV of  $\text{RbNO}_3$  (ref. 68). Rubidium and Oxygen atoms are in an approximate cubic-close-packed arrangement; their distribution among the three superposed layers shown is indicated by dark, light and dashed circles.





○ Oxygen atom  
 ○ Nitrogen atom

Fig. 5. 15 Structure of  $\text{RbNO}_3$  in cubic phase III (following Korhonen<sup>11</sup>). The Rubidium ions are at the corners of the small cubes (not shown) and  $\text{NO}_3^-$  ions are shown on the body diagonals of the small cubes. The plane of  $\text{NO}_3^-$  ion is perpendicular to the body diagonal.

conductivity at this transformation is very large and hence the orientational disordering of  $\text{NO}_3$  group may not alone be responsible for this. The suggestion of Brown and McLaren<sup>(4)</sup> is that this large increase in electrical conductivity may be due to the randomization of the  $\text{Rb}^+$  ions at this transformation. The latter proposal has been made on the basis of the following considerations.

The crystallographic relationship between phases II and I of  $\text{TlNO}_3$  is analogous to that existing between phases IV and III of  $\text{RbNO}_3$ . This is clear from the following comparative study of  $\text{TlNO}_3$  and  $\text{RbNO}_3$ <sup>(16)</sup>.



- |   |   |
|---|---|
| (i) Electrical conductance increases by a factor of 100 at II $\rightarrow$ I transformation.   | (i) Corresponding increase is by a factor of 1000 at IV $\rightarrow$ III transformation.                       |
| (ii) Phase II is hexagonal with $a=10.47\text{\AA}$ <sup>o</sup> $c=7.52\text{\AA}$ <sup>o</sup> and $Z=9$ .  | (ii) Phase IV is trigonal with $a=10.49\text{\AA}$ <sup>o</sup> , $c=7.44\text{\AA}$ <sup>o</sup> and $Z = 9$ . |
| (iii) Five lines in the X-ray powder pattern of phase I in the range $15^\circ < 2\theta < 50^\circ$ are identical with five strongest lines in the pattern | (iii) Four lines in the X-ray powder diffraction pattern of phases III and IV as given in table 5.13            |

of phase II, the slight shift to lower Bragg angles is due to the thermal expansion. are similarly identical, with a slight shift in Bragg angles due to thermal expansion.

Rowland and Bromberg<sup>(77)</sup> show by thallium magnetic resonance that  $Tl^+$  ion has mobility in phase I as high as in the melt of  $TlNO_3$ . This suggests that large increase in conductance at  $II \rightarrow I$  transformation in  $TlNO_3$  is due to the positional disorder of  $Tl^+$  ion

TABLE 5.13 'd' values and indices of four similar lines in phases IV and III of  $TbNO_3$ .

Phase IV (Temperature 124°C)		Phase III (Temperature 170°C)	
d(Å)	h kl	d(Å)	h kl
4.308	111	4.347	100
3.044	300	3.074	110
2.509	221	2.509	111
1.935	303	1.944	210

therefore, it seems reasonable to assume that, associated

with the orientational disordering of the  $\text{NO}_3^-$  ions is some amount of positional randomization of the  $\text{Rb}^+$  ions. This hypothesis receives support from the following observation (section 1.3) of Kennedy<sup>(17)</sup> (Chaplin and Kennedy). On annealing phase III (after  $\text{IV} \rightarrow \text{III}$  transformation) for 20 hours, changes in X-ray reflections correspond to changes of 20 to 40% in the ionic conductivity of  $\text{RbNO}_3$  crystals. Since the X-ray reflections are mostly affected by the positions of  $\text{Rb}^+$  ions, therefore, about 40% of the change in conductivity might be due to the randomization of  $\text{Rb}^+$  ions.

As seen in section 1.7 Myasnikova and Yatsenko<sup>(53)</sup> have recently reported that the internal vibrations of the  $\text{NO}_3^-$  ion in  $\text{RbNO}_3$  contribute very little to the change in dielectric constant at  $\text{IV} \rightarrow \text{III}$  transition and that the main contribution is from the structure vibrations. Dantsiger and Pesenko<sup>(26)</sup> have remarked that changes of dielectric constant at the transition temperatures do not correspond to the changes in electrical conductivity in  $\text{RbNO}_3$ . It is, therefore, clear that the change in electrical conductivity is not completely due to the positional randomization of  $\text{Rb}^+$  ions which mainly control the lattice vibrations. Hence  $\text{IV} \rightarrow \text{III}$  transformation seems to be of the order-disorder type.

While a diffuse X-ray scattering study of phase III might throw some additional light on the disordering of the  $\text{NO}_3^-$  ion, experiments on  $\text{IV} \rightarrow \text{III}$  transformation in the far-infrared region might help to find out the changes in lattice modes involving randomization of  $\text{Rb}^+$  ions during the transformation.

#### 5.5.4 $\text{III} \rightarrow \text{II}$ transformation:

We have seen in section 4.5 that no infrared absorption spectrum is observed in phase II of  $\text{RbNO}_3$ . This is explained on the basis of ordering of  $\text{NO}_3$  groups in phase II. Dantsiger<sup>(61)</sup> also proposed antiferroelectric properties in phase II on the assumption of ordering of  $\text{NO}_3$  groups.

This ordering process may be responsible for the sharp decrease in electrical conductivity at  $\text{III} \rightarrow \text{II}$  transformation. The ordering of  $\text{NO}_3$  groups is probably responsible for the observation of Kennedy<sup>(5)</sup> that recrystallization takes place in phase II after  $\text{III} \rightarrow \text{II}$  transformation. However, the suggestion of Brown and McLaren<sup>(4)</sup> is that  $\text{Rb}^+$  ions (probably) are getting ordered in phase II.

It was concluded, while explaining the difference between the thermal expansion plots obtained from dilatometric and X-ray studies (section 5.1), that preferred orientation takes

place of the  $\text{III} \rightarrow \text{II}$  transformation. This observation seems to be consistent with the reconstructive nature of this transformation as reported by Kennedy (5).

5.5.5  $\text{II} \rightarrow \text{I}$  transformation:

In the infrared absorption spectra of  $\text{PbNO}_3$  at  $285^\circ\text{C}$  (not shown in the text) the strong band at the position of fundamental mode  $\nu_2$  of  $\text{NO}_3^-$  ion in  $\text{PbNO}_3$  made a slight appearance. This band not enhanced at  $290^\circ\text{C}$  and  $294^\circ\text{C}$ .

This re-appearance of the infrared spectrum in phase I is explained (section 5.3) on the basis of gradual disordering of the  $\text{NO}_3$  groups due to the phase transition  $\text{II} \rightarrow \text{I}$  in  $\text{RbNO}_3$ . This gradual disordering process seems to be responsible for the gradual increase in electrical conductivity at this transformation. The gradual nature of this transition is also clear from dilatometric curves (uppermost curve of fig. 4.10).

Kennedy (5) has also concluded this transformation as one of gradual order-disorder. The basis of his conclusion is the progressive fading of some of the X-ray reflections and changes in the intensity of others as the transformation  $\text{I} \rightarrow \text{II}$  is traversed in (probably) single crystals of  $\text{RbNO}_3$ .

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# APPENDIX

A<sub>1</sub>

## A. Calculation of Heat of Transition $\Delta H$ from the DTA Peak.

Let  $m_1$  gms. of a standard material (say  $\text{RbNO}_3$  in this case) of molecular weight  $M_1$  be packed in one of the holes of the metal block of DTA apparatus. The quantity of heat released by  $\frac{m_1}{M_1}$  moles of the standard material is  $\frac{m_1}{M_1} H$  cal., where  $H$  cal./mole is the heat of transformation of the standard material. This quantity of heat is represented by area  $A_1$  of the DTA peak for  $\text{RbNO}_3$ .

Let the other hole of the metal block of the DTA apparatus be packed by an equal volume of the sample substance (solid solutions in this case). Let the weight of the substance taken be  $m_2$  gms and molecular weight be  $M_2$ .

Therefore  $\frac{m_2}{M_2}$  moles of the substance correspond to an area  $A_2$  of the DTA peak.  $A_2$  is equivalent to  $H \frac{m_1}{M_1} \frac{A_2}{A_1}$  cal. of heat. This heat is released by  $\frac{m_2}{M_2}$  moles of the substance.

Therefore one mole will release  $H \frac{m_1 A_2}{m_2 A_1} \frac{M_2}{M_1}$  or

$$\Delta H = H \frac{m_1 A_2}{m_2 A_1} \frac{M_2}{M_1}$$

## B. Calculation of Energy of Activation $E_a$ from the DTA Curves

Rate constant of a reaction (or thermal transformation) is given by (Arrhenius rate equation)

$$k = C e^{-E_a/RT}$$

$$\text{or } \log_e k = -E_a/RT + \log_e C \quad (1)$$

where  $E_a$  is the energy of activation for the transformation,

$R$  the gas constant,  $T$  the absolute temperature and  $C$  is a

constant.  $\log k$  at different temperatures are calculated

from the DTA peak and a plot of  $\log k$  vs  $1/T$ , called the

activation energy plot, is obtained. From the slope of this

plot, which is a straight line plot,  $E_a$  is calculated.

From (1),

$$\frac{E_a}{2.303R} = \text{Slope of activation energy plot}$$

$$E_a = 2.303 R (\text{Slope of activation energy plot}).$$

C. Calculation of the Magnification of the Dilatometer.

Let O, S and T (fig (b)) represent the

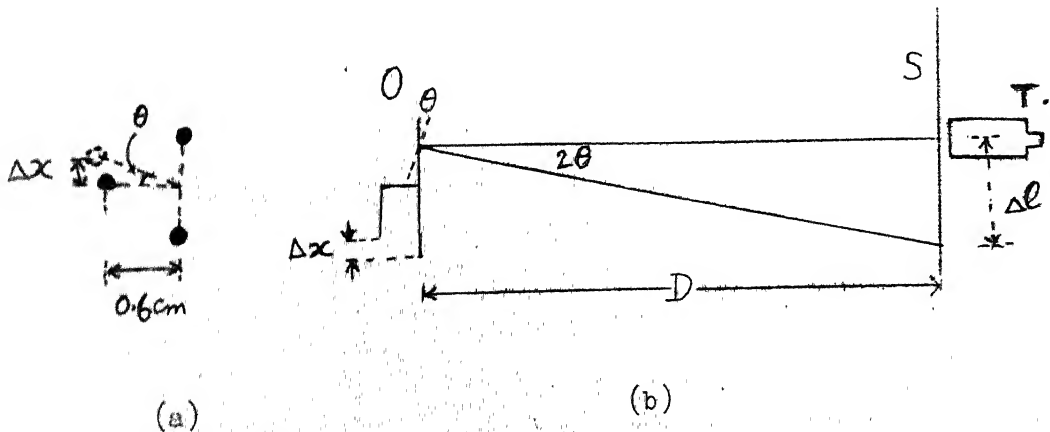


Fig. Optical lever arrangement in the dilatometric experiment

optical lever, vertical scale and the telescope respectively

in the dilatometric experiment The solid circles in fig (a) represent the foot prints of the optical lever.

Suppose the central leg of the optical lever is displaced (from solid circle to open circle fig.(a) vertically by a distance  $\Delta l$ . This tilts the mirror of the optical lever (fig (b) by an angle  $\theta$  resulting in a shift of  $2\theta$  for the optical beam from the telescope. From the geometry of the figure (b) it is evident that

$$\tan 2\theta = \frac{\Delta l}{D}$$

where  $2\theta$  and  $D$  are shown in the figure. Since  $2\theta$  is very small, we can write

$$2\theta = \frac{\Delta l}{D}$$

$$\therefore \theta = \frac{\Delta l}{2D}$$

Also from fig (a),

$$\theta = \frac{\Delta x}{0.6}$$

where 0.6 cm is the distance shown in the figure.

$$\therefore \Delta x = 0.6 (\theta)$$

$$= 0.6 \frac{\Delta l}{2D}$$

The distance  $D$ , between the optical lever and the scale, was measured as 136 cm in the experimental set up.

$$\therefore \Delta x = 0.6 \frac{\Delta l}{2 \times 136}$$

$$\therefore \text{Magnification} = \frac{\Delta l}{\Delta x} = \frac{2 \times 136}{0.6}$$

## D. Conductivity Data.

TABLE. D1. Conductivity data during heating and cooling for  $\text{RbNO}_3$ 

$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	Conductivity ( $\text{I-cm})^{-1}$ Heating	$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	Conductivity ( $\text{I-cm})^{-1}$ Cooling
403	2.4814	$1.68 \times 10^{-7}$	405	2.4690	$3.19 \times 10^{-7}$
413	2.4213	1.83 "	407	2.4570	3.48 "
423	2.3641	3.17 "	409	2.4440	4.17 "
427	2.3419	3.57 "	413	2.4213	5.49 "
429	2.3310	4.39 "	415	2.4096	7.06 "
430	2.3250	6.80 "	417	2.3981	$1.19 \times 10^{-6}$
431	2.3202	9.52 "	418	2.3920	1.66 "
432	2.3140	$1.90 \times 10^{-6}$	419	2.3866	2.72 "
433	2.3095	7.52 "	420	2.3800	9.06 "
434	2.3040	$2.83 \times 10^{-5}$	421	2.3753	$2.30 \times 10^{-5}$
435	2.2989	5.29 "	422	2.3690	$1.97 \times 10^{-4}$
436	2.2930	7.52 "	423	2.3641	2.34 "
437	2.2883	$2.04 \times 10^{-4}$	425	2.3529	2.94 "
438	2.2830	2.38 "	427	2.3419	3.36 "
439	2.2779	2.38 "	429	2.3310	3.57 "
441	2.2670	2.86 "	433	2.3095	4.28 "
443	2.2573	3.17 "	443	2.2573	6.54 "
445	2.2472	3.57 "	453	2.2075	9.83 "

$T(^{\circ}\text{K}) \quad \frac{1000}{T}(^{\circ}\text{K})^{-1} \quad \text{Conductivity } (\text{cm})^{-1}$ Heating			$T(^{\circ}\text{K}) \quad \frac{1000}{T}(^{\circ}\text{K})^{-1} \quad \text{Conductivity } (\text{cm})^{-1}$ Cooling		
447	2.2371	$4.08 \times 10^{-4}$	463	2.1598	$1.41 \times 10^{-3}$
453	2.2075	5.71 "	467	2.1413	1.61 "
463	2.1598	6.50 "	471	2.1231	1.88 "
473	2.1142	$1.19 \times 10^{-3}$	472	2.1180	1.96 "
483	2.0704	1.59 "	473	2.1142	1.97 "
493	2.0450	2.04 "	474	2.1090	2.04 "
503	2.0284	2.28 "	475	2.1053	$5.10 \times 10^{-4}$
515	2.0202	2.38 "	476	2.1000	3.17 "

$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	Conductivity (Ohm-cm) <sup>-1</sup>	$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	Conductivity (Ohm-cm) <sup>-1</sup>
Heating			Cooling		
496	2.0100	$2.38 \times 10^{-3}$	477	2.0964	$1.10 \times 10^{-4}$
497	2.0121	2.42 "	479	2.0877	$3.64 \times 10^{-5}$
498	2.0080	2.28 "	480	2.083	2.74 "
499	2.0040	$5.49 \times 10^{-4}$	481	2.0790	1.48 "
500	2.0000	2.13 "	483	2.0704	1.26 "
501	1.9960	1.14 "	489	2.0450	1.45 "
502	1.9920	$7.71 \times 10^{-5}$	493	2.0284	1.61 "
503	1.9881	4.86 "	497	2.0121	1.83 "
504	1.984	3.86 "	503	1.9881	2.16 "
505	1.9802	3.08 "	507	1.9724	2.46 "
506	1.976	2.28 "	511	1.9569	2.77 "
507	1.9724	2.30 "	513	1.9493	2.93 "
513	1.9493	2.36 "	514	1.9450	3.04 "
519	1.9268	2.67 "	515	1.9417	3.10 "
523	1.9120	2.60 "	516	1.9370	3.24 "
525	1.9048	3.04 "	517	1.9342	3.36 "
526	1.9010	3.14 "	519	1.9269	3.48 "
527	1.8975	3.21 "	521	1.9194	3.64 "
528	1.8930	3.28 "	522	1.9150	3.76 "



$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	Conductivity ( $\text{Ohm-cm}$ ) <sup>-1</sup> Heating	$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	Conductivity ( $\text{Ohm-cm}$ ) <sup>-1</sup> Cooling
529	1.8934	$3.36 \times 10^{-5}$	523	1.9120	$3.91 \times 10^{-5}$
533	1.8762	3.81 "	524	1.9080	4.08 "
535	1.8691	4.08 "	525	1.9048	4.20 "
539	1.8553	4.61 "	526	1.9010	4.33 "
543	1.8416	5.10 "	527	1.8975	4.46 "
549	1.8215	6.42 "	528	1.8930	4.61 "
551	1.8149	7.32 "	529	1.8904	4.76 "
552	1.8110	7.52 "	530	1.8860	$4.84 \times 10^{-5}$
553	1.8083	8.40 "	531	1.8832	4.92 "
554	1.8050	8.93 "	532	1.8790	5.15 "
555	1.8018	$1.02 \times 10^{-4}$	533	1.8762	5.39 "
556	1.7980	1.10 "	534	1.8720	5.60 "
557	1.7953	1.30 "	535	1.8691	6.21 "
558	1.7920	2.04 "	536	1.8650	6.42 "
559	1.7889	2.38 "	537	1.8622	6.64 "
560	1.7850	2.36 "	538	1.8580	6.88 "
561	1.7825	2.91 "	539	1.8553	7.14 "
562	1.7790	3.24 "	540	1.8510	7.72 "
563	1.7762	3.24 "	541	1.8484	8.40 "

$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	$\frac{\text{Conductivity}}{(\text{Ohm-cm})^{-1}}$ Heating	$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	$\frac{\text{Conductivity}}{(\text{Ohm-cm})^{-1}}$ Cooling
564	1.7730	$3.52 \times 10^{-4}$	543	1.8416	$1.26 \times 10^{-4}$
567	1.7637	-	547	1.8282	2.72 "
571	1.7513	$8.05 \times 10^{-4}$	553	1.8083	$1.78 \times 10^{-3}$
573	1.7452	8.93 "	557	1.7953	2.13 "
575	1.7391	$1.19 \times 10^{-3}$	563	1.7762	3.62 "
577	1.7331	3.24 "	573	1.7452	$4.39 \times 10^{-2}$
579	1.7271	6.35 "	575	1.7391	5.95 "
581	1.7212	$1.63 \times 10^{-2}$	579	1.7271	6.21 "
583	1.7153	3.17 "	583	1.7153	4.76 "

TABLE.D2 Conductivity data during heating and cooling for  
 $0.05^{Rb}0.95^{NO_3}$

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ω <sup>-1</sup> cm) <sup>-1</sup>	
		Heating	Cooling
373	2.6809	1.08x10 <sup>-7</sup>	-
393	2.5445	1.06 "	1.37x10 <sup>-7</sup>
403	2.4814	1.10 "	1.31 "
407	2.4570	1.04 "	1.34 "
411	2.4331	1.08 "	1.37 "
413	2.4213	1.03 "	-
415	2.4096	1.01 "	1.48 "
417	2.3981	1.06 "	1.63 "
419	2.3866	1.10 "	1.60 "
421	2.3753	1.08 "	1.71 "
423	2.3641	1.14 "	1.86 "
425	2.4529	1.07 "	1.97 "
427	2.3419	1.10 "	2.18 "
429	2.3310	1.17 "	2.48 "
431	2.3202	1.23 "	3.14 "
433	2.3095	1.26 "	4.86 "
435	2.2989	1.37 "	7.14 "
437	2.2883	1.43 "	1.80x10 <sup>-6</sup>

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ω <sup>-1</sup> cm) <sup>-1</sup>	
		Heating	Cooling
439	2.2779	4.28x10 <sup>-7</sup>	6.28x10 <sup>-5</sup>
441	2.2676	5.14x10 <sup>-6</sup>	1.85x10 <sup>-4</sup>
443	2.2573	1.40x10 <sup>-5</sup>	2.34 "
445	2.2472	1.97 "	2.63 "
447	2.2371	2.37 "	2.94 "
449	2.2271	2.66 "	3.14 "
451	2.2173	2.97 "	3.71 "
453	2.2075	3.43 "	4.00 "
463	2.1598	5.14x10 <sup>-5</sup>	6.28x10 <sup>-4</sup>
473	2.1142	7.43 "	9.43 "
483	2.0704	1.06x10 <sup>-4</sup>	1.26x10 <sup>-3</sup>
493	2.0284	1.57 "	1.74 "
503	1.9881	2.14 "	2.31 "
507	1.9724	2.46 "	2.57 "
511	1.9569	2.77 "	2.86 "
513	1.9493	2.94 "	2.97 "
515	1.9417	3.11 "	3.08 "
517	1.9342	3.43 "	3.43 "
519	1.9268	3.48 "	3.54 "
521	1.9194	3.48 "	3.54 "

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ω <sup>-1</sup> cm) <sup>-1</sup>	
		Heating	Cooling
523	1.9120	1.28x10 <sup>-4</sup>	3.71x10 <sup>-3</sup>
525	1.9048	1.37 "	1.71 "
527	1.8975	1.00 "	4.28x10 <sup>-4</sup>
529	1.8904	7.74x10 <sup>-5</sup>	7.14 "
531	1.8832	5.74 "	5.71 "
533	1.8762	4.28 "	4.28 "
535	1.8691	3.71 "	3.71 "
537	1.8622	3.43 "	3.43 "
543	1.8416	2.31 "	2.28 "
547	1.8282	1.94 "	1.91 "
551	1.8149	1.60 "	1.68 "
553	1.8083	1.57 "	1.68 "
555	1.8018	1.56 "	1.60 "
557	1.7953	1.57 "	1.48 "
559	1.7889	1.59x10 <sup>-5</sup>	1.48x10 <sup>-4</sup>
561	1.7825	1.74 "	1.57 "
563	1.7762	2.23 "	2.34 "
565	1.7699	3.71 "	2.54 "

T(°K)	$\frac{100}{T}$ (°K) <sup>-1</sup>	Conductivity (cm) <sup>-1</sup>	
		Heating	Cooling
567	1.7637	4.57x10 <sup>-5</sup>	3.43x10 <sup>-4</sup>
569	1.7575	5.71 "	4.86 "
571	1.7513	8.00 "	6.86 "
573	1.7452	-	1.34x10 <sup>-3</sup>
575	1.7391	-	3.71 "
577	1.7331	-	8.28 "
579	1.7271	-	1.06x10 <sup>-2</sup>
581	1.7212	-	1.66 "
583	1.7153	-	1.91 "
585	1.7094	-	2.14 "
587	1.7036	-	2.34 "
589	1.6978	-	2.51 "
591	1.6920	-	2.54 "
593	1.6863	-	2.57 "
595	1.6807	-	2.63 "
597	1.6750	-	2.71 "
599	1.6694	-	2.71 "
601	1.6639	-	2.71 "
603	1.6584	-	2.83 "

TABLE D3. Conductivity data during heating and cooling for  
 $0.10\text{Rb}0.90\text{NO}_3$ .

$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	Conductivity Heating ( $\mu\text{S cm}^{-1}$ )	$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	Conductivity Cooling ( $\mu\text{S cm}^{-1}$ )
393	2.5445	$1.23 \times 10^{-7}$	393	2.5445	$1.54 \times 10^{-7}$
403	2.4814	1.26 "	403	2.4814	1.89 "
413	2.4213	1.34 "	405	2.4690	2.20 "
417	2.3981	1.40 "	407	2.4570	2.57 "
419	2.3866	1.48 "	409	2.4450	2.86 "
421	2.3753	1.60 "	411	2.4331	3.71 "
423	2.3641	1.74 "	413	2.4213	4.28 "
425	2.3529	1.86 "	415	2.4096	5.14 "
427	2.3419	2.46 "	417	2.3981	6.00 "
429	2.3310	3.43 "	419	2.3866	6.86 "
431	2.3202	6.00 "	421	2.3753	8.28 "
433	2.3095	$1.34 \times 10^{-6}$	423	2.3641	$1.17 \times 10^{-6}$
435	2.2989	$1.23 \times 10^{-5}$	425	2.3529	1.63 "
437	2.2883	8.57 "	427	2.3419	3.14 "
439	2.2779	$1.08 \times 10^{-4}$	429	2.3310	$2.28 \times 10^{-5}$
441	2.2676	1.23 "	431	2.3202	5.71 "
443	2.2573	1.31 "	433	2.3095	8.00 "

$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	$\frac{\text{Conductivity}}{\text{Heating (11-cm)}^{-1}}$	$T(^{\circ}\text{K})$	$\frac{1000}{T}(^{\circ}\text{K})^{-1}$	$\frac{\text{Conductivity}}{\text{Cooling (11-cm)}^{-1}}$
453	2.2075	$2.00 \times 10^{-4}$	435	2.2989	$1.00 \times 10^{-4}$
463	2.1598	3.14 "	439	2.2779	1.23 "
473	2.1142	4.86 "	443	2.2573	1.48 "
483	2.0704	7.14 "	453	2.2075	2.28 "
493	2.0284	9.91 "	463	2.1598	3.43 "
503	1.9881	$1.41 \times 10^{-3}$	473	2.1142	5.43 "
515	1.9493	2.06 "	483	2.0704	7.71 "
523	1.9120	2.60 "	493	2.0284	$1.14 \times 10^{-3}$
527	1.8975	2.91 "	503	1.9881	1.51 "
531	1.8832	$3.25 \times 10^{-3}$	513	1.9493	$2.14 \times 10^{-3}$
533	1.8762	3.43 "	517	1.9342	2.46 "
535	1.8691	3.62 "	519	1.9268	2.43 "
537	1.8622	3.68 "	521	1.9194	2.23 "
539	1.8553	2.22 "	523	1.9120	1.88 "
541	1.8484	1.29 "	525	1.9048	1.54 "
543	1.8416	$8.57 \times 10^{-4}$	527	1.8975	1.28 "
547	1.8282	5.40 "	529	1.8904	1.06 "
551	1.8143	4.06 "	531	1.8832	$9.14 \times 10^{-4}$



$T(^{\circ}\text{K})$	$\frac{1000}{T} (^{\circ}\text{K})^{-1}$	Conductivity Heating ( $\text{W cm}^{-1}$ )	$T(^{\circ}\text{K})$	$\frac{1000}{T} (^{\circ}\text{K})^{-1}$	Conductivity Cooling ( $\text{W cm}^{-1}$ )
553	1.8083	$3.48 \times 10^{-4}$	533	1.8762	$7.43 \times 10^{-4}$
557	1.7953	2.38 "	535	1.8691	5.31 "
559	1.7889	3.03 "	537	1.8622	2.59 "
561	1.7825	$1.14 \times 10^{-3}$	539	1.8553	1.57 "
563	1.7762	2.43 "	541	1.8484	1.14 "
565	1.7699	2.71 "	543	1.8416	1.06 "
567	1.7637	$1.51 \times 10^{-2}$	547	1.8282	1.06 "
569	1.7575	1.94 "	551	1.8149	1.28 "
571	1.7513	2.20 "	553	1.8083	1.57 "
573	1.7452	2.31 "	555	1.8018	3.14 "
575	1.7391	2.54 "	557	1.7953	8.06 "
577	1.7331	2.94 "	559	1.7889	$2.57 \times 10^{-3}$
579	1.7271	2.87 "	561	1.7825	$1.20 \times 10^{-2}$
581	1.7212	3.11 "	563	1.7762	1.48 "
583	1.7153	3.14 "	565	1.7699	1.86 "
-	-	-	567	1.7637	2.14 "
-	-	-	569	1.7575	2.51 "
-	-	-	571	1.7513	$2.71 \times 10^{-2}$

-----  
 $T(^{\circ}K)$      $\frac{1000}{T} (^{\circ}K)^{-1}$      $\frac{\text{Conductivity}}{\text{Heating } (1 - \alpha_m)^{-1}}$      $T(^{\circ}K)$      $\frac{1000}{T} (^{\circ}K)^{-1}$      $\frac{\text{Conductivity}}{\text{Cooling } (1 - \alpha_m)^{-1}}$   
 -----

-	-	-	573	1.7452	$2.80 \times 10^{-2}$
-	-	-	575	1.7391	2.36 "
-	-	-	577	1.7331	2.88 "
-	-	-	579	1.7271	3.00 "
-	-	-	581	1.7212	3.14 "
-	-	-	583	1.7153	3.14 "

TABLE D.4 Conductivity data during heating and cooling for  
 $\text{Cs}_{0.20}\text{Rb}_{0.80}\text{NO}_3$

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ω <sup>-1</sup> cm) <sup>-1</sup>	
		Heating	Cooling
393	2.5445	1.14x10 <sup>-7</sup>	1.23x10 <sup>-7</sup>
403	2.4814	1.23 "	1.25 "
407	2.4570	1.31 "	1.23 "
411	2.4331	1.37 "	1.26 "
413	2.4213	1.37 "	1.31 "
415	2.4096	1.31 "	1.45 "
417	2.3981	1.31 "	-
419	2.3866	1.34 "	2.51x10 <sup>-7</sup>
421	2.3753	1.31 "	2.57 "
423	2.3641	1.31 "	8.57 "
425	2.3529	1.37 "	3.14x10 <sup>-6</sup>
427	2.3419	1.68 "	8.85 "
429	2.3310	3.43 "	2.17x10 <sup>-5</sup>
431	2.3202	9.14x10 <sup>-6</sup>	2.51 "
433	2.3095	1.83x10 <sup>-5</sup>	2.77 "
435	2.2989	2.48 "	3.17 "
437	2.2883	2.97 "	3.51 "
439	2.2779	3.43 "	3.82 "
441	2.2676	3.77 "	4.34 "
443	2.2573	4.23 "	4.85 "
453	2.2075	7.24 "	8.00 "

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity ( $\frac{\text{JL}}{\text{cm}} \cdot \text{sec}^{-1}$ )	
		Heating	Cooling
463	2.1598	1.15x10 <sup>-4</sup>	1.28x10 <sup>-4</sup>
473	2.1142	1.81 "	2.00 "
483	2.0704	2.78 "	3.14 "
493	2.0284	3.71 "	4.57 "
497	2.0121	4.57	5.14 "
501	1.9960	5.43x10 <sup>-4</sup>	6.00x10 <sup>-4</sup>
503	1.9881	5.93 "	6.57 "
507	1.9724	6.95 "	7.71 "
511	1.9569	6.51 "	8.86 "
513	1.9493	8.43 "	9.43 "
515	1.9417	8.97 "	1.00x10 <sup>-3</sup>
517	1.9342	9.33 "	1.06 "
521	1.9194	1.10x10 <sup>-3</sup>	1.23 "
523	1.9120	1.18 "	1.31 "
525	1.9048	1.25 "	1.37 "
527	1.8975	1.32 "	1.48 "
529	1.8904	1.44 "	1.57 "
531	1.8832	1.50 "	1.63 "
533	1.8762	1.60 "	1.77 "
535	1.8691	1.70 "	1.91 "
537	1.8622	1.82 "	2.00 "
539	1.8553	1.93 "	2.11 "

T(°K)	$1000/T(^{\circ}\text{K})^{-1}$	Conductivity ( $\frac{\text{cm}^2}{\text{sec}}$ ) <sup>-1</sup>	
		Heating	Cooling
541	1.8484	$2.02 \times 10^{-3}$	$2.23 \times 10^{-3}$
543	1.8416	2.19 "	1.65 "
545	1.8349	2.28 "	1.68 "
547	1.8282	2.39 "	1.68 "
549	1.8215	2.54 "	1.51 "
551	1.8149	2.73 "	-
553	1.8083	2.85 "	-
555	1.8018	3.03 "	$2.28 \times 10^{-3}$
557	1.7953	3.08 "	2.85 "
559	1.7889	$3.07 \times 10^{-3}$	$5.43 \times 10^{-3}$
561	1.7825	3.50 "	9.14 "
563	1.7762	4.41 "	$1.26 \times 10^{-2}$
565	1.7699	8.57 "	1.97 "
567	1.7637	$1.48 \times 10^{-2}$	2.31 "
569	1.7575	1.91 "	2.34 "
571	1.7513	2.17 "	2.37 "
573	1.7452	2.25 "	2.43 "
575	1.7391	2.40 "	2.43 "
577	1.7331	2.45 "	2.57 "
579	1.7271	2.48 "	2.60 "
581	1.7212	2.57 "	2.57 "
583	1.7153	2.57 "	2.57 "

TABLE D.5 Conductivity data during heating and cooling for  
 $\text{Cs}_{0.25}\text{Rb}_{0.75}\text{NO}_3$

$T(^{\circ}\text{K})$	$1000/T(^{\circ}\text{K})^{-1}$	Conductivity ( $\Omega^{-1}\text{cm}^{-1}$ ) <sup>-1</sup>	
		Heating	Cooling
393	2.5445	$1.11 \times 10^{-7}$	$1.14 \times 10^{-7}$
403	2.4814	1.14 "	1.23 "
407	2.4570	1.14 "	1.43 "
411	2.4331	1.23 "	4.28 "
413	2.4213	1.21 "	8.57 "
417	2.3981	1.26 "	$5.14 \times 10^{-6}$
419	2.3866	1.31 "	9.14 "
421	2.3753	1.34 "	$1.20 \times 10^{-5}$
423	2.3641	1.43 "	1.37 "
425	2.3529	1.48 "	1.57 "
427	2.3419	2.03 "	1.74 "
429	2.3310	4.00 "	1.94 "
431	2.3202	9.43 "	2.20 "
433	2.3095	$1.68 \times 10^{-6}$	2.46 "
435	2.2989	4.00 "	-
437	2.2883	6.57 "	-
439	2.2779	$1.06 \times 10^{-5}$	-
441	2.2676	1.34 "	-
443	2.2573	1.60 "	$4.28 \times 10^{-5}$
453	2.2075	3.08 "	7.14 "
463	2.1598	5.14 "	$1.14 \times 10^{-4}$

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (cm <sup>-1</sup> ) <sup>-1</sup>	
		Heating	Cooling
473	2.1142	8.25x10 <sup>-5</sup>	1.77x10 <sup>-4</sup>
483	2.0704	1.34x10 <sup>-4</sup>	2.60 "
493	2.0284	2.14 "	4.00 "
503	1.9881	3.14 "	6.00 "
513	1.9493	5.14 "	8.57 "
523	1.9120	7.43x10 <sup>-4</sup>	1.17x10 <sup>-3</sup>
533	1.8762	1.06x10 <sup>-3</sup>	1.77 "
537	1.8622	1.20 "	2.28 "
541	1.8484	1.34 "	3.43 "
543	1.8416	1.46 "	7.43 "
545	1.8349	1.54 "	9.71 "
547	1.8282	1.66 "	1.26x10 <sup>-2</sup>
549	1.8215	1.77 "	1.40 "
551	1.8149	1.86 "	1.57 "
553	1.8083	1.97 "	1.74 "
555	1.8018	2.06 "	1.86 "
557	1.7953	2.23 "	1.88 "
559	1.7889	2.40 "	1.94 "
561	1.7825	2.77 "	2.00 "
563	1.7762	3.43 "	2.00 "
565	1.7699	4.00 "	2.11 "
567	1.7637	8.57 "	2.08 "

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ω <sup>-1</sup> cm) <sup>-1</sup>	
		Heating	Cooling
569	1.7575	1.14x10 <sup>-2</sup>	2.11x10 <sup>-2</sup>
571	1.7513	1.40 "	2.17 "
573	1.7452	1.54 "	2.23 "
575	1.7391	1.66 "	2.17 "
577	1.7331	1.77 "	2.14 "
579	1.7271	1.86 "	2.2 "
581	1.7212	1.91 "	2.2 "
583	1.7153	2.06 "	2.20 "
-	-	-	-



TABLE D6 Conductivity data on Cs<sub>0.30</sub>Rb<sub>0.70</sub>NO<sub>3</sub>

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
393	2.5445	1.14x10 <sup>-7</sup>	1.23x10 <sup>-7</sup>
403	2.4814	1.28 "	1.31 "
407	2.4570	1.28 "	2.31 "
411	2.4331	1.40 "	6.28 "
413	2.4213	1.46 "	1.06x10 <sup>-6</sup>
415	2 4096	1.51 "	2.17 "
417	2.3981	1.54 "	5.14 "
419	2 3866	1.60 "	1.03x10 <sup>-5</sup>
421	2.3753	1 80 "	1.34 "
423	2.3641	2 34 "	1.57 "
425	2.3529	4 00 "	1.86 "
427	2.3419	1.54x10 <sup>-6</sup>	2.08 "
429	2.3310	5.43 "	2.36 "
431	2.3202	9.71 "	2.66 "
433	2.3095	1.20x10 <sup>-5</sup>	2.86 "
435	2 2989	1.34 "	3.43 "
437	2 2883	1.54 "	3.71 "
439	2 2779	1.74 "	4 28 "
441	2 2676	2.06 "	4.86 "
443	2 2573	2 28 "	5.14 "
453	2 2075	3.71 "	8.86 "
463	2.1598	6.28 "	1.48x10 <sup>-4</sup>
473	2.1142	1.06x10 <sup>-4</sup>	2.37 "
483	2 0704	1.71 "	3.71 "
493	2.0284	2.71 "	5.43 "
503	1.9881	4.00 "	8.00 "

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
513	1.9493	6.28x10 <sup>-4</sup>	1.14x10 <sup>-3</sup>
523	1.9120	9.14 "	1.60 "
527	1.8975	1.06x10 <sup>-3</sup>	1.80 "
529	1.8904	1.11 "	1.91 "
531	1.8832	1.20 "	2.06 "
533	1.8762	1.36 "	2.23 "
535	1.8691	1.46 "	2.37 "
537	1.8622	1.51 "	2.51 "
539	1.8553	1.60 "	2.66 "
541	1.8484	1.71 "	2.83 "
543	1.8416	1.83 "	2.80 "
545	1.8344	1.94 "	3.14 "
547	1.8282	2.06 "	3.71 "
549	1.8215	2.17 "	4.57 "
551	1.8149	2.31 "	6.28 "
553	1.8083	2.51 "	9.14 "
555	1.8018	2.63 "	1.23x10 <sup>-2</sup>
557	1.7953	2.83 "	1.51 "
559	1.7889	3.08 "	1.68 "
561	1.7825	3.43 "	1.83 "
563	1.7762	4.57 "	1.88 "
565	1.7699	7.43 "	2.00 "
567	1.7637	8.71 "	2.08 "
569	1.7575	1.11x10 <sup>-2</sup>	2.08 "
571	1.7513	1.37 "	2.11 "
573	1.7452	1.57 "	2.31 "

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
575	1.7391	1.80x10 <sup>-2</sup>	2.20x10 <sup>-2</sup>
577	1.7331	1.91 "	2.20 "
579	1.7271	2.06 "	2.20 "
581	1.7212	2.06 "	2.26 "
583	1.7153	2.06 "	2.26 "

TABLE D7 Conductivity data on  $K_{0.02}Rb_{0.98}NO_3$ 

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
393	2.5445	1.11x10 <sup>-7</sup>	1.17x10 <sup>-7</sup>
395	2.5316	1.11 "	-
397	2.5188	1.11 "	-
399	2.5062	1.11 "	-
401	2.4937	1.11 "	-
403	2.4814	1.11 "	1.17x10 <sup>-7</sup>
405	2.4691	1.11 "	-
407	2.4570	1.14 "	-
409	2.4449	1.14 "	1.20x10 <sup>-7</sup>
411	2.4331	1.11 "	1.17 "
413	2.4213	1.14 "	1.17 "
415	2.4096	1.14 "	1.26 "
417	2.3981	1.11 "	1.37 "
419	2.3866	1.11 "	1.46 "
421	2.3753	1.20 "	2.28 "
423	2.3641	1.24 "	5.71x10 <sup>-6</sup>
425	2.3529	1.28 "	6.57x10 <sup>-5</sup>
427	2.3419	1.43 "	1.40x10 <sup>-4</sup>
429	2.3310	1.43 "	1.80 "
431	2.3202	1.54 "	1.97 "
433	2.3095	1.60 "	2.14 "
435	2.2989	1.91 "	2.37 "
437	2.2883	3.71 "	2.57 "
439	2.2779	6.86 "	2.86 "
441	2.2676	3.26x10 <sup>-6</sup>	3.14 "
443	2.2573	4.57x10 <sup>-5</sup>	3.43 "

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
445	2.2472	-	3.71x10 <sup>-4</sup>
447	2.2371	1.71x10 <sup>-4</sup>	4.00 "
449	2.2272	2.26 "	4.57 "
451	2.2173	2.71 "	4.57 "
453	2.2075	3.03 "	2.28 "
455	2.1978	3.43 "	8.57x10 <sup>-5</sup>
457	2.1882	3.71 "	3.71 "
459	2.1786	4.00 "	1.43 "
461	2.1692	4.28 "	5.43x10 <sup>-6</sup>
463	2.1598	4.57 "	2.66 "
465	2.1505	4.86 "	2.14 "
467	2.1413	5.14 "	2.08 "
469	2.1322	5.71 "	2.11 "
471	2.1231	6.00 "	2.23 "
473	2.1142	6.57 "	2.40 "
475	2.1053	6.86 "	2.57 "
477	2.0964	7.43 "	2.74 "
479	2.0877	8.00 "	2.86 "
481	2.0790	8.57 "	3.14 "
483	2.0704	9.14 "	3.43 "
485	2.0619	9.43 "	3.71 "
487	2.0534	9.43 "	4.00 "
489	2.0450	8.57 "	4.28 "
491	2.0367	6.57 "	4.57 "
493	2.0284	3.71 "	4.86 "
495	2.0202	1.71 "	5.43 "

$T(^{\circ}\text{K})$	$1000/T(^{\circ}\text{K})^{-1}$	<u>Conductivity (Ohm-cm)<sup>-1</sup></u>	
497	2.0121	$1.08 \times 10^{-4}$	$5.71 \times 10^{-6}$
499	2.0040	$7.71 \times 10^{-5}$	6.00 "
501	1.9960	5.43 "	6.57 "
503	1.9881	3.43 "	6.86 "
505	1.9802	2.00 "	7.43 "
507	1.9724	1.37 "	8.00 "
509	1.9646	1.11 "	8.57 "
511	1.9569	1.03 "	9.14 "
513	1.9493	1.03 "	9.71 "
515	1.9417	1.06 "	$1.03 \times 10^{-5}$
517	1.9342	1.06 "	1.08 "
519	1.9268	1.08 "	1.14 "
521	1.9194	1.14 "	1.23 "
523	1.9120	1.20 "	1.31 "
525	1.9048	1.26 "	1.43 "
527	1.8975	1.34 "	1.54 "
529	1.8904	1.40 "	1.63 "
531	1.8832	1.48 "	1.74 "
533	1.8762	1.60 "	1.86 "
535	1.8691	1.68 "	2.08 "
537	1.8622	1.80 "	2.26 "
539	1.8553	1.91 "	2.43 "
541	1.8484	2.03 "	2.57 "
543	1.8416	2.17 "	4.57 "
545	1.8349	2.31 "	8.00 "
547	1.8282	2.43 "	$1.11 \times 10^{-4}$

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
549	1.8215	2.57x10 <sup>-5</sup>	2.00x10 <sup>-4</sup>
551	1.8149	2.77 "	3.43 "
553	1.8083	2.97 "	7.14 "
555	1.8018	3.43 "	1.26x10 <sup>-3</sup>
557	1.7953	3.71 "	1.66 "
559	1.7889	4.28 "	-
561	1.7825	4.86 "	2.20x10 <sup>-3</sup>
563	1.7762	6.86 "	2.28 "
565	1.7699	8.28 "	4.28 "
567	1.7637	9.43 "	6.00 "
569	1.7575	1.08x10 <sup>-4</sup>	1.00x10 <sup>-2</sup>
571	1.7513	1.28 "	1.34 "
573	1.7452	1.60 "	1.80 "
575	1.7391	2.08 "	2.11 "
577	1.7331	3.26 "	2.57 "
579	1.7271	5.71 "	2.86 "
581	1.7212	1.08x10 <sup>-3</sup>	3.14 "
583	1.7153	1.40 "	3.14 "
585	1.7094	1.88 "	3.14 "
587	1.7036	4.28 "	3.14 "
589	1.6978	8.28 "	-
591	1.6920	2.40x10 <sup>-2</sup>	-
593	1.6863	-	3.43x10 <sup>-2</sup>
595	1.6807	3.71x10 <sup>-2</sup>	3.43 "
597	1.6750	3.43 "	3.43 "
599	1.6694	3.43 "	3.43 "
601	1.6639	3.43 "	3.43 "
603	1.6584	3.43 "	3.43 "

TABLE D.8 Conductivity data on  $K_{0.04}Rb_{0.96}NO_3$ 

$T(^{\circ}K)$	$1000/T (^{\circ}K)^{-1}$	$\frac{\text{Conductivity (Ohm-cm)}^{-1}}{\text{Heating Cooling}}$	
		Heating	Cooling
393	2.5445	$1.26 \times 10^{-7}$	$1.40 \times 10^{-7}$
395	2.5316	1.26 "	1.43 "
397	2.5188	1.23 "	1.46 "
399	2.5062	1.26 "	1.51 "
401	2.4937	1.26 "	1.57 "
403	2.4814	1.28 "	1.94 "
405	2.4691	1.26 "	2.40 "
407	2.4570	1.26 "	2.66 "
409	2.4449	1.28 "	2.86 "
411	2.4331	1.34 "	3.14 "
413	2.4213	1.31 "	3.43 "
415	2.4096	1.28 "	3.71 "
417	2.3981	1.28 "	4.57 "
419	2.3866	1.28 "	8.86 "
421	2.3753	1.37 "	$2.28 \times 10^{-6}$
423	2.3641	1.43 "	$4.00 \times 10^{-5}$
425	2.3529	1.48 "	7.43 "
427	2.3419	1.51 "	7.14 "
429	2.3310	1.57 "	4.83 "
431	2.3202	1.68 "	2.80 "
433	2.3095	1.86 "	1.34 "
435	2.2989	2.17 "	$6.57 \times 10^{-6}$
437	2.2883	4.00 "	2.54 "
439	2.2779	$4.57 \times 10^{-6}$	1.77 "
441	2.2676	$2.60 \times 10^{-5}$	1.48 "
443	2.2573	8.0 "	1.34 "



T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
445	2.2472	1.40x10 <sup>-4</sup>	1.28x10 <sup>-6</sup>
447	2.2371	1.63 "	1.26 "
449	2.2272	1.86 "	1.26 "
451	2.2173	2.06 "	1.28 "
453	2.2075	2.23 "	1.31 "
455	2.1978	2.40 "	1.37 "
457	2.1882	2.57 "	1.46 "
459	2.1786	2.68 "	1.54 "
461	2.1692	2.80 "	1.66 "
463	2.1598	2.86 "	1.80 "
465	2.1505	2.83 "	1.94 "
467	2.1413	2.54 "	2.08 "
469	2.1322	2.40 "	2.20 "
471	2.1231	2.37 "	2.37 "
473	2.1142	2.31 "	2.57 "
475	2.1053	2.28 "	2.77 "
477	2.0964	2.23 "	3.00 "
479	2.0877	2.11 "	3.14 "
481	2.0790	1.91 "	3.43 "
483	2.0704	1.77 "	3.71 "
485	2.0619	1.60 "	4.00 "
487	2.0534	1.46 "	4.57 "
489	2.0450	1.28 "	4.86 "
491	2.0367	1.06 "	5.14 "
493	2.0284	8.86x10 <sup>-5</sup>	5.43 "
495	2.0202	6.86 "	5.71 "

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
497	2.0121	5.43x10 <sup>-5</sup>	6.0x10 <sup>-6</sup>
499	2.0040	3.71 "	6.28 "
501	1.9960	2.57 "	6.86 "
503	1.9881	1.80 "	7.43 "
505	1.9802	1.43 "	7.71 "
507	1.9724	1.20 "	8.57 "
509	1.9646	1.11 "	9.14 "
511	1.9569	1.08 "	1.00x10 <sup>-5</sup>
513	1.9493	1.08 "	1.06 "
515	1.9417	1.11 "	1.14 "
517	1.9342	1.14 "	1.23 "
519	1.9268	1.17 "	1.31 "
521	1.9194	1.20 "	1.37 "
523	1.9120	1.26 "	1.48 "
525	1.9048	1.31 "	1.57 "
527	1.8975	1.37 "	1.68 "
529	1.8904	1.43 "	2.00 "
531	1.8832	1.48 "	2.26 "
533	1.8762	1.54 "	2.43 "
535	1.8691	1.63 "	2.63 "
537	1.8622	1.71 "	3.14 "
539	1.8553	1.83 "	4.00 "
541	1.8484	1.94 "	5.43 "
543	1.8416	2.06 "	6.86 "
545	1.8349	2.17 "	9.43 "
547	1.8282	2.34 "	1.23x10 <sup>-4</sup>
549	1.8215	2.48 "	1.77 "

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
551	1.8149	2.68x10 <sup>-5</sup>	3.71x10 <sup>-4</sup>
553	1.8083	2.26 "	6.57 "
555	1.8018	3.14 "	1.48x10 <sup>-3</sup>
557	1.7953	3.71 "	2.00 "
559	1.7889	4.28 "	-
561	1.7825	5.71 "	3.43x10 <sup>-3</sup>
563	1.7762	8.86 "	6.00 "
565	1.7699	1.11x10 <sup>-4</sup>	9.14 "
567	1.7637	1.31 "	1.23x10 <sup>-2</sup>
569	1.7575	1.51 "	1.57 "
571	1.7513	1.63 "	1.83 "
573	1.7452	2.00 "	1.97 "
575	1.7391	2.83 "	2.06 "
577	1.7331	4.28 "	2.23 "
579	1.7271	8.28	2.28 "
581	1.7212	4.00x10 <sup>-3</sup>	2.34 "
583	1.7153	6.00 "	2.31 "
585	1.7094	8.00 "	2.40 "
587	1.7036	1.17x10 <sup>-2</sup>	2.46 "
589	1.6978	2.03 "	2.54 "
591	1.6920	2.34 "	2.54 "
593	1.6863	2.71 "	2.57 "
595	1.6807	2.46 "	2.51 "
597	1.6750	2.57 "	2.63 "
599	1.6694	2.63 "	2.68 "
601	1.6639	2.66 "	2.74 "
603	1.6584	2.68	2.77 "

TABLE D.9 Conductivity data on  $K_{0.05}Rb_{0.95}NO_3$ 

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
393	2.5445	1.34x10 <sup>-7</sup>	3.71x10 <sup>-7</sup>
403	2.4814	1.66 "	3.43 "
407	2.4570	1.91 "	4.00 "
411	2.4331	2.11 "	4.57 "
413	2.4213	2.25	4.57 "
415	2.4096	2.43	5.14 "
417	2 3981	3.14 "	5.14 "
419	2.3866	3.43 "	5.71 "
421	2.3753	3.71 "	6.00 "
423	2.3641	4.28 "	7.71 "
425	2.3529	4.57 "	2.00x10 <sup>-6</sup>
427	2.3419	4.86 "	3.43 "
429	2.3310	5.43 "	1.28 "
431	2.3202	6.57 "	7.71x10 <sup>-7</sup>
433	2 3095	1.14x10 <sup>-6</sup>	7.43
435	2.2989	8.57 "	7.43 "
437	2.2883	4.00x10 <sup>-5</sup>	7.43 "
439	2.2779	6.80 "	7.71 "
441	2.2676	1.03x10 <sup>-4</sup>	7.71 "
443	2.2573	1.34 "	8.00 "

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
445	2.2472	1.54x10 <sup>-4</sup>	8.43x10 <sup>-7</sup>
447	2.2371	1.63 "	8.57 "
449	2.2272	1.66 "	8.86 "
451	2.2173	1.71 "	9.71 "
453	2.2075	1.74 "	1.03x10 <sup>-6</sup>
455	2.1978	1.75 "	1.11 "
457	2.1882	1.78 "	1.20 "
459	2.1786	1.74 "	1.31 "
461	2.1692	1.72 "	1.43 "
463	2.1598	1.52 "	1.51 "
465	2.1505	1.59 "	1.63 "
467	2.1413	1.53 "	1.74 "
469	2.1322	1.41 "	1.88 "
471	2.1231	1.27 "	2.03 "
473	2.1142	1.14 "	2.20 "
475	2.1053	1.03 "	2.37 "
477	2.0964	8.86x10 <sup>-5</sup>	2.54 "
479	2.0877	7.83 "	2.77 "
481	2.0790	6.28 "	3.14 "
483	2.0704	4.00 "	3.43 "
485	2.0619	2.86 "	3.71 "
487	2.0534	2.00 "	3.71 "
489	2.0450	1.66 "	4.00 "
491	2.0367	1.26 "	4.26 "
493	2.0284	8.86x10 <sup>-6</sup>	4.57 "
495	2.0202	7.71 "	5.14 "

$T(^{\circ}\text{K})$	$1000/T(^{\circ}\text{K})^{-1}$	Conductivity ( $\text{Ohm-cm}$ ) <sup>-1</sup>	
		Heating	Cooling
497	2.0121	$7.14 \times 10^{-6}$	$5.43 \times 10^{-6}$
499	2.0040	6.86 "	5.71 "
501	1.9960	7.14 "	6.00 "
503	1.9881	7.20 "	6.57 "
505	1.9802	7.34 "	7.43 "
507	1.9724	7.51 "	8.00 "
509	1.9646	7.63 "	8.57 "
511	1.9569	7.91 "	8.86 "
513	1.9493	8.20 "	9.71 "
515	1.9417	8.51 "	$1.06 \times 10^{-5}$
517	1.9342	8.83 "	1.11 "
519	1.9268	9.20 "	1.20 "
521	1.9194	9.60 "	1.28 "
523	1.9120	$1.01 \times 10^{-5}$	1.37 "
525	1.9048	1.06 "	1.48 "
527	1.8975	1.13 "	1.60 "
529	1.8904	1.19 "	1.74 "
531	1.8832	1.23 "	1.38 "
533	1.8762	1.32 "	2.06 "
535	1.8691	1.41 "	2.20 "
537	1.8622	1.47 "	2.57 "
539	1.8553	1.55 "	3.43 "
541	1.8484	1.64 "	4.28 "
543	1.8416	1.75 "	5.43 "
545	1.8349	1.85 "	7.43 "
547	1.8282	1.98 "	$1.03 \times 10^{-4}$
549	1.8215	2.10 "	1.57 "

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
551	1.8149	2.28x10 <sup>-5</sup>	2.57x10 <sup>-4</sup>
553	1.8083	2.86 "	3.43 "
555	1.8018	3.71 "	4.00 "
557	1.7953	4.80 "	4.22 "
559	1.7889	5.37 "	4.57 "
561	1.7825	5.23 "	5.14 "
563	1.7762	6.66 "	6.57 "
565	1.7699	5.86 "	1.37x10 <sup>-3</sup>
567	1.7637	7.34 "	2.43 "
569	1.7575	1.08x10 <sup>-4</sup>	-
571	1.7513	1.45 "	2.73x10 <sup>-1</sup>
573	1.7452	3.08	2.76 "
575	1.7391	5.14 "	2.30 "
577	1.7331	8.00 "	2.30 "
579	1.7271	1.48x10 <sup>-3</sup>	2.34 "
581	1.7212	3.14x10 <sup>-1</sup>	2.40 "
583	1.7153	3.11 "	2.39 "
585	1.7094	1.11 "	2.40 "
587	1.7036	1.14 "	2.40 "
589	1.6978	1.14 "	2.40 "
591	1.6920	1.17 "	2.40 "
593	1.6863	2.43 "	2.47 "
595	1.6807	2.43 "	2.46 "
597	1.6750	2.43 "	2.45 "
599	1.6694	2.43 "	2.44 "
601	1.6639	2.43 "	2.44 "
603	1.6584	2.43 "	2.43 "

Table D.10 Conductivity data on  $\text{K}_{0.07}\text{Rb}_{0.93}\text{NO}_3$ .

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
393	2.5445	1.94x10 <sup>-7</sup>	2.34x10 <sup>-7</sup>
395	2.5316	2.06 "	2.48 "
397	2.5188	2.11 "	2.54 "
399	2.5062	2.83 "	2.77 "
401	2.4927	3.14 "	2.83 "
403	2.4814	3.71 "	2.88 "
405	2.4691	4.00 "	2.94 "
407	2.4570	4.57 "	2.97 "
409	2.4449	5.14 "	3.03 "
411	2.4331	5.43 "	2.94 "
413	2.4213	6.00 "	2.94 "
415	2.4096	6.86 "	3.14 "
417	2.3981	7.71 "	3.14 "
419	2.3866	8.57 "	3.71 "
421	2.3753	9.71 "	4.57 "
423	2.3641	1.08x10 <sup>-6</sup>	4.86 "
425	2.3529	1.26 "	5.14 "
427	2.3419	1.40 "	5.43 "
429	2.3310	1.60 "	5.71 "
431	2.3202	1.83 "	6.00 "
433	2.3095	2.51 "	6.57 "
435	2.2989	3.71 "	6.86 "
437	2.2883	1.14x10 <sup>-5</sup>	7.43 "
439	2.2779	2.74 "	8.00 "
441	2.2676	5.71 "	8.28 "
443	2.2573	1.14x10 <sup>-4</sup>	8.86 "



T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
445	2.2472	1.34x10 <sup>-4</sup>	9.43x10 <sup>-7</sup>
447	2.2371	1.43 "	1.03x10 <sup>-6</sup>
449	2.2272	1.48 "	1.11 "
451	2.2173	1.54 "	1.23 "
453	2.2075	1.57 "	1.28 "
455	2.1978	1.57 "	1.43 "
457	2.1882	1.57 "	1.51 "
459	2.1786	1.54 "	1.63 "
461	2.1692	1.51 "	1.74 "
463	2.1598	1.43 "	1.91 "
465	2.1505	1.37 "	2.06 "
467	2.1413	1.26 "	2.20 "
469	2.1322	1.20 "	2.40 "
471	2.1231	1.11 "	2.60 "
473	2.1142	1.00 "	2.74 "
475	2.1053	8.86x10 <sup>-5</sup>	3.03 "
477	2.0964	8.00 "	3.14 "
479	2.0877	6.86 "	3.43 "
481	2.0790	5.71 "	3.71 "
483	2.0704	4.86 "	4.00 "
485	2.0619	4.00 "	4.28 "
487	2.0534	3.14 "	4.86 "
489	2.0450	2.28 "	5.14 "
491	2.0367	1.74 "	5.43 "
493	2.0284	1.40 "	5.71 "
495	2.0202	1.11 "	6.28 "

T(°K)	1000/T(°K) <sup>-1</sup>	Conductivity (Ohm-cm) <sup>-1</sup>	
		Heating	Cooling
497	2.0121	9.71x10 <sup>-6</sup>	6.57x10 <sup>-6</sup>
499	2.0040	9.14 "	7.14 "
501	1.9960	9.14 "	7.71 "
503	1.9881	9.43 "	8.28 "
505	1.9802	9.71 "	8.86 "
507	1.9724	1.03x10 <sup>-5</sup>	9.43 "
509	1.9646	1.06 "	1.03x10 <sup>-5</sup>
511	1.9569	1.14 "	1.08 "
513	1.9493	1.20 "	1.20 "
515	1.9417	1.28 "	1.26 "
517	1.9342	1.34 "	1.37 "
519	1.9268	1.40 "	1.46 "
521	1.9194	1.46 "	1.54 "
523	1.9120	1.57 "	1.68 "
525	1.9048	1.66 "	1.83 "
527	1.8975	1.77 "	2.00 "
529	1.8904	1.86 "	2.14 "
531	1.8832	1.97 "	2.3k "
533	1.8762	2.11 "	2.60 "
535	1.8691	2.23 "	2.94 "
537	1.8622	2.37 "	3.43 "
539	1.8553	2.48 "	4.57 "
541	k,8484	2.66 "	7.43 "
543	1.3416	2.88 "	9.71 "
545	1.8349	3.08 "	1.28x10 <sup>-4</sup>
547	1.8282	3.43 "	1.68 "
549	1.8215	3.43 "	2.57 "

$T(^{\circ}\text{K})$	$1000/T (^{\circ}\text{K})^{-1}$	<u>Conductivity (Ohm-cm)<sup>-1</sup></u>	
		Heating	Cooling
551	1.8149	$3.71 \times 10^{-5}$	$3.43 \times 10^{-4}$
553	1.8083	4.28 "	6.00 "
555	1.8018	4.86 "	$1.23 \times 10^{-3}$
557	1.7953	7.14 "	2.57 "
559	1.7889	$1.51 \times 10^{-4}$	4.00 "
561	1.7825	2.06 "	6.28 "
563	1.7762	2.40 "	8.86 "
565	1.7699	2.54 "	$1.31 \times 10^{-2}$
567	1.7637	2.54 "	1.77 "
569	1.7575	2.68 "	2.17 "
571	1.7513	4.57 "	2.40 "
573	1.7452	8.28 "	2.63 "
575	1.7391	$1.00 \times 10^{-3}$	2.74 "
577	1.7331	2.28 "	2.86 "
579	1.7271	8.00 "	2.86 "
581	1.7212	$1.74 \times 10^{-2}$	2.86 "
583	1.7153	2.28 "	2.86 "
585	1.7094	-	2.86 "
587	1.7036	$3.03 \times 10^{-2}$	2.86 "
589	1.6978	2.86 "	-
591	1.6920	2.86 "	-
593	1.6863	2.86 "	$3.14 \times 10^{-2}$
595	1.6807	2.86 "	3.14 "
597	1.6750	3.14 "	3.14 "
599	1.6694	3.14 "	3.14 "
601	1.6639	3.14 "	3.14 "
603	1.6584	3.14 "	3.14 "

## E. DTA data

TABLE : E1 Thermal hysteresis data derived from DTA curves (figs. 4.5 or 4.6 at  $x = 0$ ) of  $\text{RbNO}_3$  for  $\text{IV} \rightleftharpoons \text{III}$  and  $\text{III} \rightleftharpoons \text{II}$  transformations.

IV $\rightleftharpoons$ III				III $\rightleftharpoons$ II			
Heating		Cooling		Heating		Cooling	
Temperature (°C)	Fraction transformed	Temperature (°C)	Fraction transformed	Temperature (°C)	Fraction transformed	Temperature (°C)	Fraction transformed
160.0	0.00	158.0	1.00	220.0	0.00	213.5	1.00
162.0	0.00	156.5	0.93	222.5	0.07	212.0	0.91
165.0	0.15	156.0	0.83	223.5	0.20	211.5	0.83
165.5	0.25	156.0	0.73	225.5	0.32	211.0	0.63
167.0	0.46	156.0	0.63	226.0	0.44	210.5	0.52
168.0	0.62	156.0	0.48	228.0	0.67	210.0	0.36
169.0	0.78	156.0	0.33	230.0	0.91	209.5	0.21
170.0	0.90	156.0	0.18	231.5	1.00	208.0	0.12
170.5	1.00	155.5	0.07			207.0	0.05
		154.0	0.03			204.0	0.00
		152.0	0.00				

TABLE E2 : Thermal hysteresis data derived from DTA curves (fig.4.5 at  $x = 0.05$ ) of  $\text{Cs}_{0.05}\text{Rb}_{0.95}\text{NO}_3$  system for  $\text{IV} \rightleftharpoons \text{III}$  and  $\text{III} \rightleftharpoons \text{II}$  transformations.

IV $\rightleftharpoons$ III				III $\rightleftharpoons$ II			
Heating		Cooling		Heating		Cooling	
Tempera- ture( $^{\circ}\text{C}$ )	Fraction transformed	Tempera- ture( $^{\circ}\text{C}$ )	Fraction transformed	Tempera- ture( $^{\circ}\text{C}$ )	Fraction transformed	Tempera- ture( $^{\circ}\text{C}$ )	Fraction transformed
158.0	0.00	155.0	1.00	240.0	0.00	229.5	1.00
160.0	0.015	154.5	0.92	244.0	0.06	228.0	0.98
161.0	0.10	154.5	0.83	244.5	0.15	228.0	0.73
161.5	0.20	154.5	0.70	245.5	0.31	227.5	0.57
162.5	0.30	154.0	0.55	246.0	0.49	227.0	0.41
164.0	0.50	153.5	0.42	247.0	0.64	226.0	0.25
164.0	0.60	153.0	0.28	248.0	0.82	225.0	0.10
164.5	0.745	152.0	0.15	249.5	1.00	220.0	0.00
165.5	0.84	150.0	0.05				
167.0	0.935	144.0	0.00				
169.5	1.00						

TABLE B3. Thermal hysteresis data derived from DTA curves (fig 4.5, at  $x = 0.10$ ) of  $\text{Cs}_{0.10}\text{Rb}_{0.90}\text{NO}_3$  system for  $\text{IV} \rightleftharpoons \text{III}$  and  $\text{III} \rightleftharpoons \text{II}$  transformations.

IV $\rightleftharpoons$ III				III $\rightleftharpoons$ II			
Heating		Cooling		Heating		Cooling	
Tempera- ture( $^{\circ}\text{C}$ )	Fraction transformed	Tempera- ture( $^{\circ}\text{C}$ )	Fraction transformed	Tempera- ture( $^{\circ}\text{C}$ )	Fraction transformed	Tempera- ture( $^{\circ}\text{C}$ )	Fraction transformed
154.0	0.00	152.0	1.00	258.0	0.00	244.0	1.00
157.5	0.02	150.5	0.95	260.0	0.01	242.0	0.92
159.0	0.05	150.0	0.87	261.5	0.07	242.0	0.79
160.0	0.14	150.0	0.74	262.0	0.14	241.0	0.65
161.0	0.27	149.5	0.62	262.5	0.27	240.0	0.44
162.0	0.35	149.0	0.46	263.5	0.41	238.0	0.24
162.5	0.44	148.0	0.34	264.0	0.54	236.0	0.10
163.0	0.53	147.0	0.22	265.5	0.68	233.5	0.03
163.5	0.62	145.5	0.14	267.0	0.82	230.0	0.00
164.0	0.71	144.5	0.06	269.0	0.93		
165.0	0.80	143.0	0.03	270.0	1.00		
165.5	0.88	138.0	0.00				
166.5	1.00						

## F. Dilatometric data

TABLE F.1 - Dilatometric data on thermal expansion of  $\text{RbNO}_3$ . Length of rod specimen ( $L$ ) = 1.5 cm

HEATING				COOLING			
Temperature (°C)	$\frac{\Delta L}{L} \times 10^3$	Temperature (°C)	$\frac{\Delta L}{L} \times 10^3$	Temperature (°C)	$\frac{\Delta L}{L} \times 10^3$	Temperature (°C)	$\frac{\Delta L}{L} \times 10^3$
81	2.93	211	30.58	275	76.78	199	56.76
91	3.81	213	36.30	273	76.71	197	52.36
101	4.75	215	42.90	271	76.56	195	47.52
111	5.65	217	50.16	269	76.34	193	41.14
121	6.53	219	57.49	267	75.90	191	39.60
131	7.55	221	63.14	265	75.24	189	39.38
141	8.65	223	65.78	263	74.80	181	38.13
151	9.75	225	66.66	261	74.14	171	36.30
153	10.34	227	67.10	259	73.77	161	34.54
155	11.22	233	67.98	257	73.48	155	33.29
157	12.98	239	68.71	255	72.75	153	32.96
159	15.55	245	69.45	249	71.72	151	31.90
161	18.33	251	70.18	243	71.06	149	30.36
163	19.80	257	70.77	237	70.40	147	28.45
165	20.24	263	71.65	231	69.89	145	27.35
167	20.68	265	72.53	225	69.37	141	26.55
175	21.93	267	73.55	219	68.79	131	25.52
185	23.54	269	74.21	213	68.20	121	24.49
195	25.08	271	74.95	207	67.61	111	23.61
205	26.69	273	76.12	205	67.39	101	22.73
207	27.06	275	76.56	203	64.97	91	21.85
209	27.65	277	76.78	201	61.45	81	20.90

TABLE F.2 - Dilatometric data on thermal expansion of Cs<sub>0.05</sub>Rb<sub>0.95</sub>NO<sub>3</sub>  
 Length of rod specimen ( $l$ ) = 1.5 cm

HEATING				COOLING			
Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$
82	3.96	206	23.83	268	69.37	206	26.11
92	4.91	216	25.37	264	69.15	200	24.49
102	5.87	226	26.77	260	68.79	190	23.03
112	6.89	230	27.57	256	68.20	180	21.41
122	7.77	232	28.75	252	67.39	170	19.95
132	8.80	234	31.60	248	66.00	160	18.43
142	9.83	236	38.13	244	64.83	152	17.30
152	10.85	238	44.15	240	64.09	150	16.72
154	11.29	240	50.60	236	63.36	148	15.62
156	12.32	242	55.00	232	62.33	146	13.20
158	13.93	244	57.49	228	60.50	144	12.03
160	15.40	246	59.25	226	59.11	142	11.66
162	17.31	250	61.60	224	57.20	140	11.29
164	17.82	254	63.21	222	54.56	130	10.34
166	18.11	258	65.19	220	51.33	122	9.61
176	19.51	262	67.03	218	47.23	112	8.73
186	20.90	266	68.49	216	41.65	102	7.99
196	22.29	270	69.30	214	35.79	92	7.19
				212	29.92	82	6.45
				210	26.55		



TABLE F.3 Dilatometric data on thermal expansion of  $\text{Cs}_{0.1}\text{Rb}_{0.9}\text{NO}_3$ .  
Length of rod specimen (l) = 1.3 cm.

HEATING				COOLING			
Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$
80.75	2.66	184.75	21.78	260.75	67.10	222.75	24.64
90.75	3.63	194.75	23.54	256.75	66.33	212.75	22.51
100.75	4.49	204.75	25.12	254.75	65.78	202.75	20.81
110.75	5.32	214.75	26.58	252.75	64.46	192.75	18.92
120.75	6.16	224.75	28.16	250.75	63.47	182.75	17.27
130.75	7.19	234.75	29.92	248.75	61.82	172.75	15.66
140.75	8.36	244.75	31.46	246.75	59.84	162.75	14.08
144.75	8.71	246.75	32.12	244.75	57.42	150.75	12.32
148.75	9.24	248.75	34.32	242.75	55.00	146.75	10.91
150.75	12.10	250.75	43.67	240.75	52.36	144.75	9.90
152.75	12.87	252.75	47.39	238.75	49.06	142.75	7.92
154.75	14.89	254.75	49.59	236.75	44.51	140.75	6.93
156.75	16.28	256.75	51.67	230.75	33.00	134.75	5.59
160.75	17.93	258.75	58.74	228.75	29.26	130.75	5.28
164.75	18.70	260.75	61.42	226.75	26.73	120.75	4.22
174.75	20.06	262.75	66.33	224.75	25.08	110.75	3.52

TABLE : F4 - Dilatometric data on thermal expansion of  $\text{Cs}_{0.20}\text{Rb}_{0.80}\text{NO}_3$ .  
Length of rod specimen (  $l$  ) = 1.3 cm

HEATING				COOLING			
Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$
80.5	3.96	156.5	18.70	250.5	31.60	142.5	13.26
90.5	4.91	162.5	19.80	246.5	31.13	140.5	13.53
100.5	5.94	172.5	21.67	236.5	29.48	136.5	12.87
110.5	6.93	182.5	22.88	226.5	27.59	134.5	12.01
120.5	7.92	192.5	24.02	216.5	25.74	132.5	11.22
130.5	9.06	202.5	25.30	206.5	23.90	126.5	8.62
134.5	9.68	212.5	26.73	196.5	22.02	122.5	7.80
140.5	11.00	222.5	27.94	186.5	20.68	110.5	6.27
142.5	12.01	232.5	29.48	176.5	18.92	100.5	5.28
146.5	15.22	242.5	30.47	166.5	17.42	90.5	4.40
148.5	17.09	252.5	31.90	156.5	15.91		
152.5	18.04			146.5	14.39		

TABLE : F.5 - Dilatometric data on thermal expansion of  $K_{0.02}Rb_{0.98}NO_3$ .  
Length of rod specimen = 1.4 cm

HEATING				COOLING			
Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$
81	3.30	207	54.34	2.75	72.99	175	36.61
91	4.09	209	57.35	271	72.69	173	29.48
101	4.84	211	59.55	269	72.29	171	25.52
111	5.72	213	60.81	265	71.35	167	24.05
121	6.60	215	62.06	261	70.55	159	22.95
131	7.48	217	62.92	257	69.74	153	21.85
141	8.36	219	63.71	251	68.86	151	21.56
151	9.58	221	64.24	245	68.20	149	20.46
153	10.35	223	64.59	239	67.76	147	18.48
155	11.88	225	64.90	231	67.19	145	16.94
157	14.74	227	65.21	221	66.46	143	15.84
159	18.04	235	66.02	211	65.78	141	15.40
161	19.14	239	66.88	201	64.90	135	14.61
163	19.49	247	67.76	191	64.04	129	14.08
169	20.59	255	68.86	187	63.36	121	13.20
175	21.56	261	69.74	185	62.48	111	12.32
181	22.40	263	70.25	183	60.81	101	11.31
187	23.41	265	70.55	181	56.32	91	10.34
193	24.22	267	71.06	179	51.04	81	9.46
195	25.30	269	71.72	177	44.88		
197	26.40	273	72.75				
199	27.81	275	73.26				
201	29.06	277	73.48				
203	34.89	279	73.70				
205	42.68	281	73.70				

TABLE: F 6 - Dilatometric data on thermal expansion of  $\text{K}_{0.04}\text{Rb}_{0.96}\text{NO}_3$   
 Length of rod specimen ( $l$ ) = 1.4 in.

HEATING				COOLING			
Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$	Temperature (°C)	$\frac{\Delta l}{l} \times 10^3$
81	4.09	191	33.79	273	61.29	171	44.79
91	5.06	193	35.35	271	61.16	169	44.00
101	5.94	195	36.96	269	60.94	167	42.90
111	6.91	197	38.72	267	60.72	165	41.01
121	7.92	199	40.55	265	60.50	163	38.28
131	8.95	201	42.46	263	60.06	161	34.32
141	9.97	203	44.44	261	59.40	159	28.91
151	11.15	205	46.35	259	58.52	157	24.86
153	11.95	207	48.71	257	57.66	155	20.46
155	13.35	209	50.75	255	57.05	153	16.50
157	16.65	211	52.36	253	56.65	151	12.76
159	17.91	213	53.68	249	55.70	149	10.21
161	18.11	215	54.34	243	54.56	147	7.55
163	18.85	217	54.91	237	53.46	145	5.65
165	19.36	219	55.31	231	52.65	143	4.25
167	19.95	221	55.46	225	51.92	141	3.52
169	20.59	225	55.88	219	51.06	139	3.15
171	21.56	231	56.54	213	50.29	133	2.20
173	22.66	237	57.05	207	49.59	127	1.56
175	23.98	243	57.66	201	48.95	121	1.01
177	24.86	249	58.17	195	48.25	111	0.00
179	25.96	255	58.74	189	47.61		
181	26.71	261	59.31	183	46.86		
183	27.94	267	60.10	177	46.05		
185	29.26	269	60.50				
187	30.80	271	60.81				
189	32.21	275	61.45				

## G. X-ray data

TABLE: G1. X-ray data on thermal expansion of  $\text{RbNO}_3$   
Phase IV (Hexagonal)

Temperature (°C)	$a_{\text{IV}} (\text{\AA})$	$c_{\text{IV}} (\text{\AA})$	$a_{\text{IV}}/6 (\text{\AA})$	$c_{\text{IV}}/3 (\text{\AA})$	$V^{1/3} = (V_{\text{IV}}/9)^{1/3} \text{\AA}$
29	10.49	7.44	4.28	4.30	4.29
54	10.51	7.46	4.29	4.31	4.30
74	10.53	7.47	4.30	4.31	4.30
97	10.55	7.49	4.31	4.32	4.31
111	10.57	7.49	4.31	4.32	4.32
124	10.58	7.50	4.32	4.33	4.32
135	10.59	7.51	4.32	4.34	4.33
139	10.59	7.52	4.32	4.34	4.33
146	10.60	7.53	4.33	4.35	4.33
153	10.62	7.52	4.34	4.34	4.34
161	10.63	7.51	4.34	4.34	4.34

Phase III		Phase II (Hexagonal)				PHASE I			
Temperature (°C)	$a_{\text{III}} (\text{\AA})$	Temperature (°C)	$a_{\text{II}} (\text{\AA})$	$c_{\text{II}} (\text{\AA})$	$\frac{a_{\text{II}}}{4}$	$\frac{c_{\text{II}}}{6}$	$V^{1/3} = \left(\frac{V_{\text{II}}}{3}\right)^{1/3}$	Temperature (°C)	$a_{\text{I}} (\text{\AA})$
170	4.347	227	5.55	10.71	4.67	4.37	4.57	286	7.32
179	4.353	232	5.54	10.75	4.66	4.39	4.57	289	7.32
191	4.358	240	5.55	10.71	4.64	4.37	4.55		
198	4.362	281	5.47	10.89	4.60	4.45	4.55		
211	4.371								
222	4.376								

TABLE : G2 X-ray data on thermal expansion of  $K_{0.04}Rb_{0.96}NO_3$ 

## Phase IV (Hexagonal)

Temperature (°C)	$a_{IV} (Å)$	$c_{IV} (Å)$	$a_{IV}/6$	$(Å)^3 c_{IV}/3$	$(Å)^3 V^{1/3} = (V_{IV/9})^{1/3} Å^3$
29	10.47	7.44	4.27	4.30	4.28
75	10.50	7.45	4.29	4.30	4.29
91	10.51	7.46	4.29	4.31	4.30
117	10.53	7.47	4.30	4.31	4.30
137	10.55	7.48	4.31	4.32	4.31
145	10.56	7.49	4.31	4.32	4.31
150	10.60	7.48	4.33	4.32	4.33
157	10.60	7.49	4.33	4.32	4.33

## Phase III

## Phase II (Hexagonal)

## Phase I

Temperature (°C)	$a_{III}$ (Å)	Temperature (°C)	$a_{II}$ (Å)	$c_{II}$ (Å)	$a_{II}/4$ (Å)	$V^{1/3} = (V_{II/3})^{1/3}$	Temperature (°C)	$a_I$ (Å)
165	4.362	192	5.56	10.72	4.68	4.38 4.58	293	7.32
167	4.357	205	5.57	10.76	4.69	4.39 4.59	296	7.33
173	4.366	256	5.55	10.82	4.67	4.42 4.58	300	7.33
185	4.373	262	5.54	10.85	4.66	4.43 4.58		
195	4.377	275	5.51	10.86	4.63	4.43 4.56		
208	4.383	283	5.48	10.93	4.61	4.46 4.56		
222	4.387	288	5.45	10.87	4.58	4.44 4.53		

TABLE : G3 X-ray data on thermal expansion of  $\text{Cs}_{0.95}\text{Rb}_{0.05}\text{NO}_3$   
Phase IV (Hexagonal)

Temperature (°C)	$a_{\text{IV}} (\text{\AA})$	$c_{\text{IV}} (\text{\AA})$	$a_{\text{IV}}/6 (\text{\AA})$	$c_{\text{IV}}/3 (\text{\AA})$	$(V_{\text{IV}})^{1/3} = (V_{\text{IV}}/9)^{1/3} (\text{\AA})$
29	10.50	7.44	4.29	4.30	4.29
56	10.52	7.45	4.29	4.30	4.29
80	10.54	7.47	4.30	4.31	4.30
100	10.56	7.47	4.31	4.31	4.31
120	10.57	7.48	4.32	4.32	4.32
132	10.59	7.49	4.32	4.33	4.32
137	10.59	7.49	4.32	4.33	4.32
145	10.60	7.51	4.33	4.34	4.33
163	10.61	7.50	4.33	4.33	4.33

Phase III			Phase II (Hexagonal)					Phase I	
Temperature (°C)	$a_{\text{III}} (\text{\AA})$	Temperature (°C)	$a_{\text{II}} (\text{\AA})$	$c_{\text{II}} (\text{\AA})$	$a_{\text{II}}/4$	$c_{\text{II}}/6$	$(V_{\text{II}})^{1/3} = (V_{\text{II}}/3)^{1/3} (\text{\AA})$	Temperature (°C)	$a_{\text{I}} (\text{\AA})$
175	4.365	244	5.52	10.77	4.64	4.40	4.56	281.5	7.31
181	4.368	248	5.52	10.75	4.64	4.39	4.56	283.0	7.32
191	4.371	255	5.51	10.77	4.63	4.40	4.55		
211	4.384	263	5.49	10.79	4.62	4.41	4.55		
224	4.398								
233	4.393								
242	4.399								